AD-A105 496 UNIVERSAL ENERGY SYSTEMS INC DAYTON OH F/G 7/4
INVESTIGATION OF PLASMA EXCITATION. VOLUME III. ADVANCED OPTICA--ETC(U)
AUG 81 C A DEJOSEPH F33615-77-C-3113
UNCLASSIFIED 707-3-F AFWAL-TR-81-2082-VOL-3 NL

1 OF 2
AD A
105496

AFWAL-TR-81-2082

INVESTIGATION OF PLASMA EXCITATION
Volume III: Advanced Optical Diagnostics

C. A. DeJoseph
Universal Energy Systems, Inc.
3195 Plainfield Road
Dayton, Ohio 45432

August 1981

Final Report for Period 7 June 1977 to 20 September 1980

Aero Propulsion Laboratory
Air Force Wright Aeronautical Laboratories
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio 45433

NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture use, or sell any patented invention that may in any way be related thereto.

This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

Gary L. Duke

GARY L. DUKE, Capt, USAF
Project Engineer

Robert R Barthelemy

ROBERT R. BARTHELEMY
Chief, Energy Conversion Branch
Aerospace Power Division

FOR THE COMMANDER

J D Reams

JAMES D. REAMS
Chief, Aerospace Power Division

"If your address has changed, if you wish to be removed from our mailing list, or if the addressee is no longer employed by your organization please notify AFWAL/POOC-3 *W-PAFB, OH 45433 to help us maintain a current mailing list".*

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: AFWAL-TR-81-2082 - VOL. III	2. GOVT ACCESSION NO.: AD-A105 496
3. RECIPIENT'S CATALOG NUMBER:	
4. TITLE: INVESTIGATION OF PLASMA EXCITATION. Volume III. Advanced Optical Diagnostics of Plasmas.	5. TYPE OF REPORT & PERIOD COVERED: Final 7 Jun[redacted]977 – 20 Sep[redacted]980
	6. PERFORMING ORG. REPORT NUMBER: 707-3-F
7. AUTHOR(s): C.A. DeJoseph	8. CONTRACT OR GRANT NUMBER(s): F33615-77-C-3113
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Universal Energy Systems, Inc. 3195 Plainfield Road Dayton, Ohio 45432	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: Program Element: 61102F Proj/Task/W.U.: 2301/S218
11. CONTROLLING OFFICE NAME AND ADDRESS: AF Wright Aeronautical Laboratories (AFWAL/POOC) Wright Patterson AFB, Ohio 45433	12. REPORT DATE: Augu[redacted]981
	13. NUMBER OF PAGES: 126
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): Unclassified
	15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Infrared Spectroscopy
Fourier Transform Spectroscopy
CO_2 Laser
Cloased Cycle Laser
Electron Beam Excited Laser
TEA CO_2 Laser
Discharge Chemistry
Carbon Monoxide

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A Fourier transform infrared spectrometer was used to identify infrared absorption spectra of impurities that might be present in CO_2 laser discharges. Spectral regions free from interference from the primary constituents and common impurities such as water vapor were identified for several of the nitrogen oxides, and the detection sensitivities were determined. This information was used in a study of impurity buildup during discharges in an electron-beam excited closed cycle (EBCC) system and in a TEA CO_2 laser.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

unclassified 340142

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

It was found that after an hour of irradiation in the continuous EBCC system, the oxides of nitrogen had built up to the ten parts per mission range while the carbon monoxide concentration was of the order of a few hundred parts per million. When the initial gas mix contained oxygen, the concentration of CO and the nitrogen oxides increased. The addition of hydrogen to an oxygen free gas mix was found to produce water vapor at about ten percent of the initial hydrogen concentration, increase the production of N_2O and of CO, and decrease the production of NO and NO_2.

A technique has been developed for determining the rotational temperature and vibrational population distribution of non-homonuclear molecules under nonequilibrium conditions. The technique was applied to carbon monoxide under the conditions present in an electrical discharge.

FOREWORD

This report describes research performed by Universal Energy Systems, Inc., Dayton, Ohio. The work was conducted under Contract F33615-77-C-3113, "Investigations of Methods of Plasma Excitation," Task III, "Advanced Optical Diagnostics of Plasmas."

The work reported herein was performed at in-house facilities of the Air Force Aero Propulsion Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio. The experimental work and analysis described was performed by C. A. DeJoseph. As Mr. DeJoseph was not employed by Universal Energy Systems at the time of the completion of the contract, this section of the final report was prepared by V. E. Merchant by combining and editing quarterly reports previously written by Mr. DeJoseph.

A

TABLE OF CONTENTS

LIST OF FIGURES

Figure		Page

LIST OF TABLES

SECTION I

INTRODUCTION

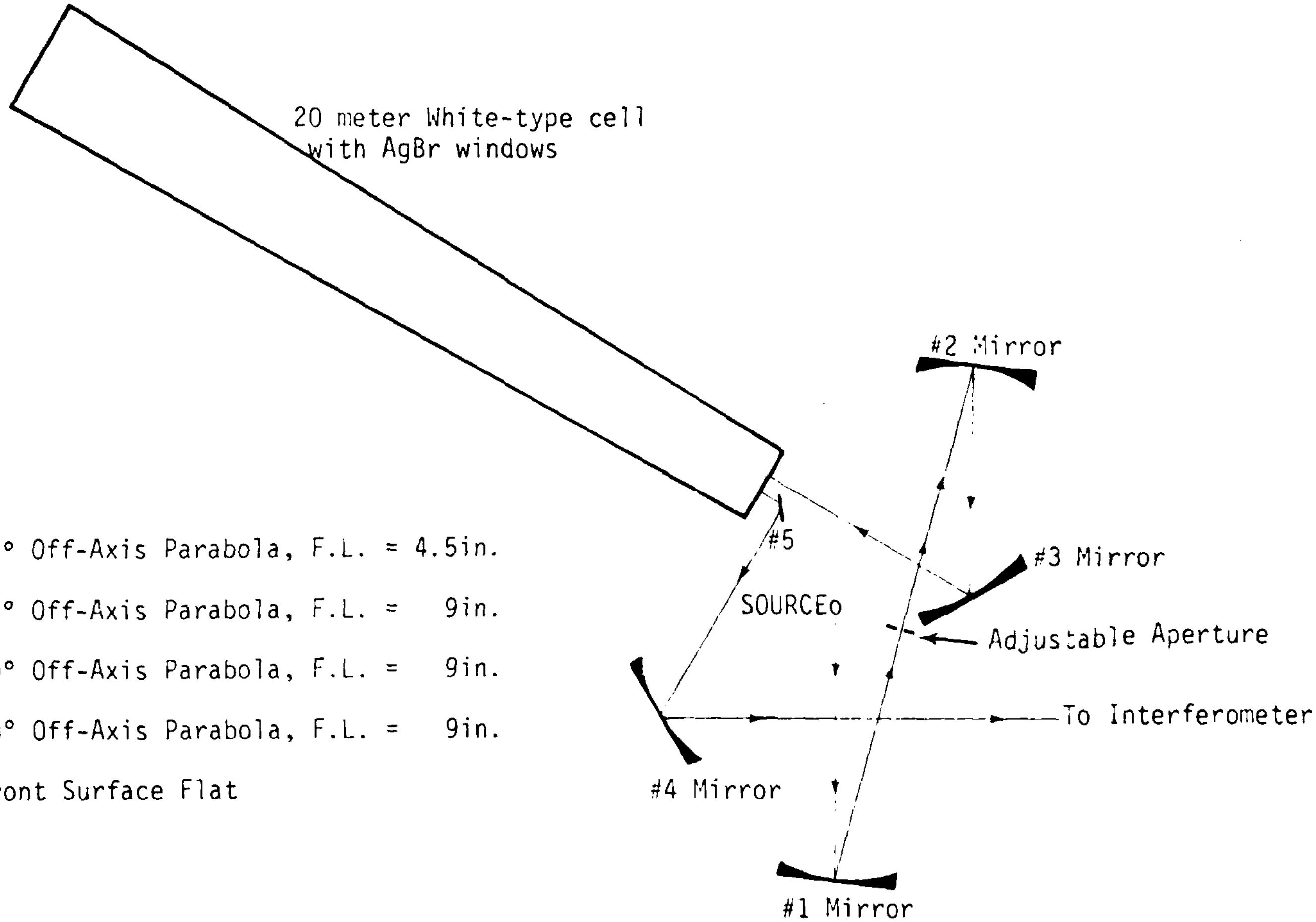
Advanced optical techniques have been applied to several problems in plasmas diagnostics. A technique has been developed for determining the rotational temperature and vibrational population distribution of non-homonuclear molecules under non-equilibrium conditions. The technique was applied to carbon monoxide under the conditions present in an electrical discharge. The second problem area was identifying infrared absorption spectra of impurities that might be present in CO_2 laser discharges. Spectral regions free from interference from the primary constituents and common impurities such as water vapor were identified for several of the nitrogen oxides, and the detection sensitivities were determined. Finally this information was used in a study of impurity buildup during discharges in an electron-beam excited closed cycle (EBCC) system and in a TEA laser.

Succeeding sections of this report give more information about the developments in these main areas of concentration. In addition several minor problems were addressed. The infrared transmittance of Freon 1301 in the 10.6 μm spectral region was investigated. Infrared emission spectra were obtained from He-Ne and He-Xe hollow cathode discharges. No further information about these minor problem areas will be given here.

Throughout the duration of the contract, several improvements were made to the Fourier Transform Spectrometer (FTS). A variable path corrosion resistant absorption cell and associated gas handling hardware were added to the system for use with corrosive gases. The system constructed for the trace species absorption measurements is centered around a long-path (20 meters) White-type infrared absorption cell with optics for use with the FTS system.

In addition, a stainless steel, high vacuum gas handling system is used for evacuating the cell and preparing the synthetic mixes. Figure 1 shows the layout of the optics system for the White cell. The glowbar source is imaged 1:1 onto the adjustable aperture by mirror #1 and then collimated by mirror #2. Mirror #3 focuses the radiation onto the entrance window of the White cell and the radiation leaving the cell is re-collimated by mirror #4. Radiation leaving mirror #4 then passes to the FTS System where the spectrum is measured. Figure 2 shows the gas handling system for the White cell. High vacuum evacuation of the system is by the liquid nitrogen trapped diffusion pump. Base pressure for the system is the mid 10^{-7} torr range. The system can be used in two ways. Samples of gas from the EBCC loop can be entered into the system via the sample port or absorption spectra of various gas mixes can be obtained by entering these into the system through the gas manifold. Gas pressure was measured with the two MKS Baratrons which gave an increase in dynamic range of pressure measurement over a single unit. Gas mixes were prepared under static pressure conditions and likewise the absorption measurements were made under static conditions. After a gas fill, the White cell was "roughed down" using forepump #2 which is a high throughput Leybold Heraeus model DK-45. Use of this pump greatly facilitated pump down of the cell from atmospheric pressure while allowing forepump #1 to remain small for reduced backstreaming to the diffusion pump.

The spectral range of study was originally limited to the range of 5.9 μm to 1.7 μm (1700-6000 cm^{-1}). This is the range over which the original PbSe detector used in the FTS System was sensitive. A new "sandwich" detector was obtained which allowed the range to be extended from 14 μm to 1.7 μm (700-6000 cm^{-1}). This detector is composed of a LN_2 cooled HgCdTe detector "sandwiched" behind a LN_2 cooled InSb detector. The detector



#1 Mirror: 15° Off-Axis Parabola, F.L. = 4.5in.

#2 Mirror: 15° Off-Axis Parabola, F.L. = 9in.

#3 Mirror: 60° Off-Axis Parabola, F.L. = 9in.

#4 Mirror: 60° Off-Axis Parabola, F.L. = 9in.

#5 Mirror: Front Surface Flat

FIGURE 1 WHITE-CELL OPTICS

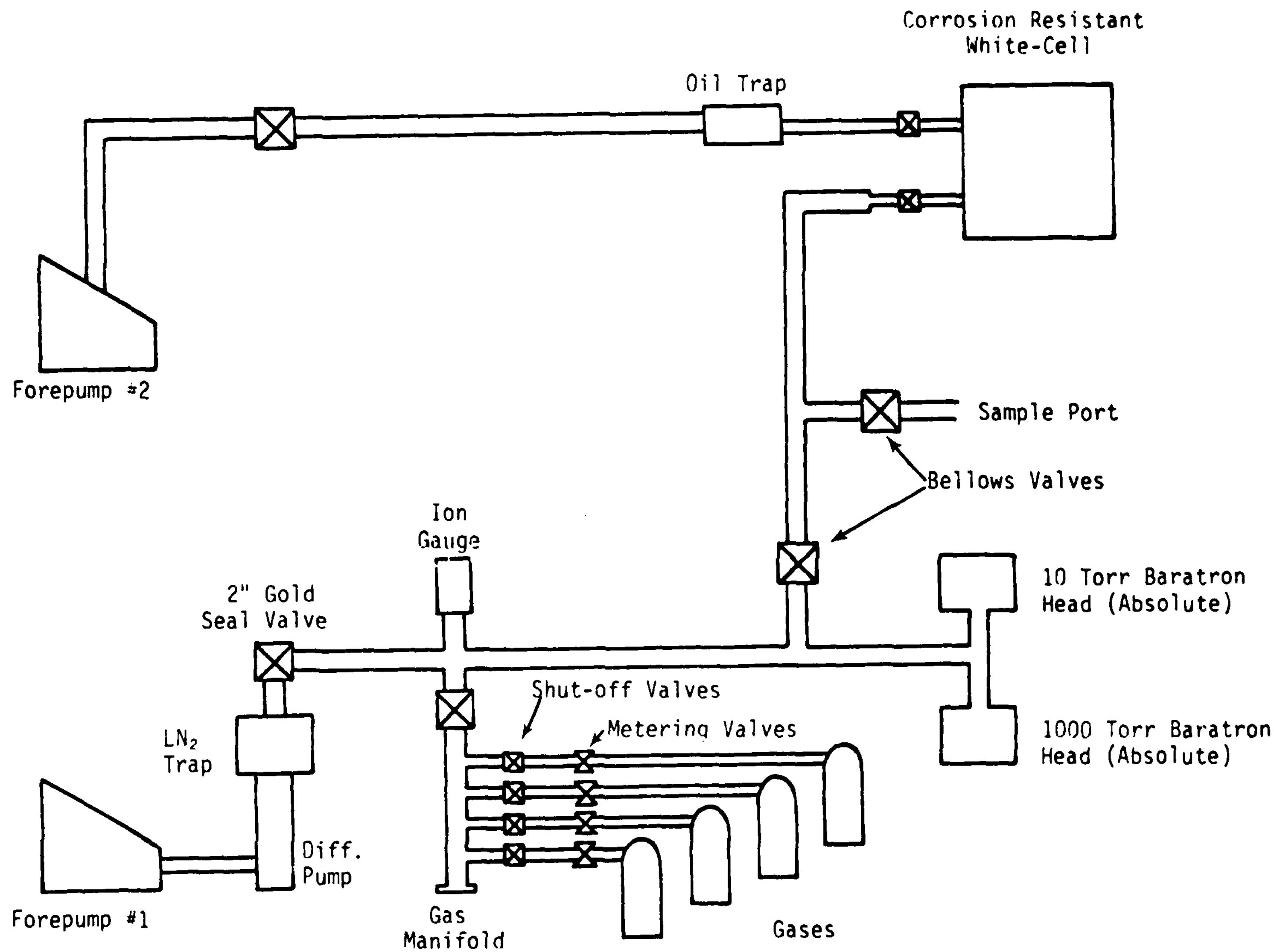


FIGURE 2 WHITE-CELL GAS HANDLING SYSTEM

can be wired so that the outputs are added or come out separately, with each configuration having its own advantages and disadvantages. For maximum signal-to-noise, the outputs are taken separately and either part of the composite detector is selected by the FTS System controller. Thus, in its present configuration the FTS System can gather data in the range of the HgCdTe detector, ie. 14 μm to 5.4 μm (700-1850 cm^{-1}) or the InSb detector, ie. 5.7 μm to 1.7 μm (1750-6000 cm^{-1}). Results shown in this report were primarily obtained with the PbSe detector. Most measurements were taken in the presence of laboratory air, so it was necessary to contend with parasitic absorption by water vapor and carbon dioxide in the air. Figure 3 shows a low resolution spectrum of the glowbar source as seen through the White cell in the InSb (or roughly the PbSe) region of the spectrum in lab air. The regions showing absorption due to H_2O and CO_2 must be taken into account when deciding where to look for absorption by the minor species. Figure 3 will serve to locate absorption features shown in more detailed spectra later in the report.

A significant change to the absorption cell-FTS optics was the installing of a germanium on potassium bromide (KBr) beamsplitter in the FTS system. With this beamsplitter and the "sandwich" detector spectral coverage of the FTS system has been extended to the range 14 μm to 2 μm. Because of the way the "sandwich" detector is wired, the spectral range must be covered in two separate data acquisitions. Data is acquired over the spectral range 14 μm to 5.4 μm (700-1850 cm^{-1}) or 5.7 μm to 2 μm (1750-5000 cm^{-1}). Thus, analysis of a gas sample requires two data acquisitions each requiring about twenty minutes to complete. Replacing the iron oxide on calcium flouride (CaF_2) beamsplitter with the KBr extends the spectral region from about 1100 cm^{-1} to 700 cm^{-1} on the low frequency side while shortening the region from

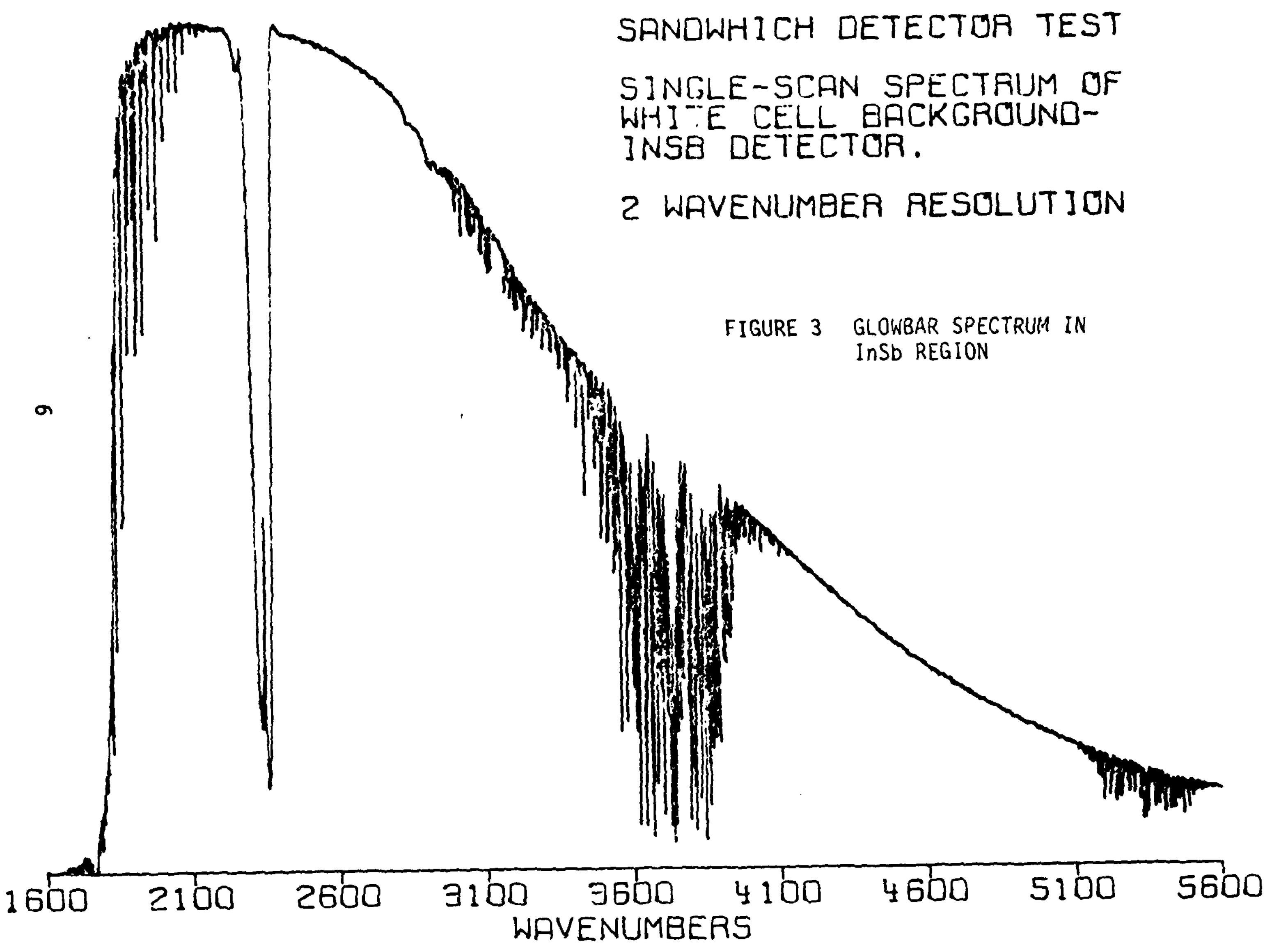


FIGURE 3 GLOWBAR SPECTRUM IN InSb REGION

6000 cm^{-1} to 5000 cm^{-1} on the high frequency side. However, due to the importance of the 10 μm spectral region in some experiments, the increased coverage in the low frequency part of the spectrum is a more desirable configuration.

An investigation was made of the factors limiting the precision of wavelength determination with the Fourier Transform Spectrometer. The precision with which a line position can be determined is dependent on a number of experimental parameters. One parameter that is fundamental to the best achievable precision is the resolution of the instrument [2]. If the only factor affecting the precision of the measurement is the experimenters ability to locate the center of the line, then the best precision achievable is likely to be between one-twentieth and one-thirtieth of the resolution [2]. The AFAPL FTS system possesses a maximum resolution of 0.6 cm^{-1} (apodized) and a theoretical resolution of .037 cm^{-1} (unapodized). Therefore, the maximum precision with which a line position can be determined with this instrument should be on the order of ±.001 and ±.003 cm^{-1}. A study was undertaken to determine how closely this maximum could be approached. Wave-number precision of the recovered spectrum from the FTS system is directly dependent on the precision with which the moving mirror position is measured in the interferogram. The mirror position is determined by monitoring the interference fringes produced by a helium-neon (HeNe) laser, so the wave-number scale in the recovered spectrum is reasonably precise due to this technique of mirror position measurement. This "automatic" calibration of the FTS-produced spectrum is sometimes referred to as Conne's advantage.

A number of factors effect the best achievable precision of this "automatic" calibration scheme so an attempt was made to identify and eliminate the largest of these. One factor effecting the precision of the calculated

wavenumbers which is well known is the degree to which radiation from the source is collimated [2]. The reason for this is that rays entering the interferometer off-axis travel a greater distance than those entering on-axis, thus the computed spectrum for the off-axis rays differs from the spectrum computed for on-axis rays. As Bell has shown [2], if the source subtends a solid angle Ω, the computed wavenumbers σ_c are related to the true wavenumbers σ_o by;

$$\sigma_c = \sigma_o (1 - \Omega/4\pi). \tag{1}$$

Thus, a measured line position will be lower in wavenumber than the true line position. Using the small angle approximation for Ω, equation (1) can be written,

$$\sigma_c = \sigma_o (1 - \alpha^2/4)$$

where α is the angle of deviation of rays entering the interferometer. For example, if one requires the wavenumbers to be within $\pm.01\ cm^{-1}$ at $4000\ cm^{-1}$, α must be 3.2 mrad. or 11 minutes of arc. Thus it is necessary when doing precision line position measurements to precisely control the degree of collimation of the source.

A second source of error results from the apparatus operating in air and the dispersion in the index of refraction of the air. Since the mirror position is measured with the HeNe laser, the wavelength of the laser serves the same purpose as a known line in a conventional spectrometer. Because the known line in the FTS system is quite removed in wavenumber from the unknown lines, the vacuum correction for the HeNe laser is not the proper correction for the IR region of the spectrum. To see this source of error more clearly, consider the fundamental equations of FT-IR. Let the fluctuating part of the interferogram as a function of path difference x be I(x), and

the spectral distribution function be $B(\sigma)$. Then for an ideal interferometer, $I(x)$ and $B(\sigma)$ are related by, ,

$$I(x) = 2\int_0^\infty B(\sigma)\cos(2\pi\sigma\ x)d\sigma \tag{2}$$

$$B(\sigma) = 2\int_0^\infty I(x)\cos(2\pi\sigma\ x)dx \tag{3}$$

where σ is in cm^{-1}, and the constant 2 is somewhat arbitrary. Assume that a source possesses a spectral distribution function (in air) of $B_o(\sigma_o)$. The measured interferogram from the source, $I_m(X_m)$, is then given by,

$$I_m(X_m) = 2\int_0^\infty B_o(\sigma_o)\ \cos\ 2\pi\sigma_o X_m d\sigma_o. \tag{4}$$

The calculated spectrum $B_c(\sigma_c)$ is given by,

$$B_c(\sigma_c) = 2\int_0^\infty I_m(X_m)\ \cos\ 2\pi\sigma_c X_c dX_c. \tag{5}$$

Substituting equation (4) into (5) gives,

$$B_c(\sigma_c) = 4\int_0^\infty \left[\int_0^\infty B_o(\sigma_o)\ \cos\ 2\pi\sigma_o X_m d\sigma_o\right] \cos\ 2\pi\sigma_c X_c dX_c. \tag{6}$$

Here the subscripts 'c' and 'm' refer to quantities either used in or the results of calculations, and quantities actually measured. The measured interferogram, I_m, is acquired by monitoring the fringes of the HeNe laser and sampling at every j^{th} zero-crossing of the laser interferogram. The laser interferogram is roughly a cosine wave which crosses zero at $X = j.\lambda/2$ where λ = HeNe and j = 1, 2, 3.... Since the laser operates in air, the measured path difference X_m is sampled with a spacing of ΔX_m given by,

$$\Delta X_m = j \cdot \tfrac{1}{2}\lambda_{Air}(\text{HeNe}),\ j = 1, 2... \tag{7}$$

where λ_{Air} is the wavelength of the helium-neon laser in air. In the calculation of $B_c(\sigma_c)$, it is assumed that the path difference was sampled

with a spacing ΔX_c given by,

$$\Delta X_c = j \cdot \tfrac{1}{2}\lambda_{Vac}(\text{HeNe}),\ j = 1, 2... \tag{8}$$

where λ_{Vac} (HeNe) is the wavelength of the helium-neon laser in vacuum. Therefore, in equation (6), X_c can be written in terms of X_m, using equations (7) and (8), as

$$X_c = \frac{\lambda_{Vac}(\text{HeNe})}{\lambda_{Air}(\text{HeNe})} \cdot X_m\ . \tag{9}$$

In equation (9) the ratio of $\lambda_{Vac}/\lambda_{Air}$ is *just the index of refraction of air at the HeNe laser wavelength.* So equation (9) becomes

$$X_c = n(\text{HeNe}) \cdot X_m \tag{10}$$

where n(HeNe) is the index of air. Using equation (10) and letting $X_m = X_c/$ n(HeNe) in equation (6) gives for the calculated spectrum,

$$B_c(\sigma_c) = 4 \cdot \int_0^\infty \left[\int_0^\infty B_o(\sigma_o) \cos 2\pi\sigma_o \frac{X_c}{n(\text{HeNe})}\, d\sigma_o \right] \cos 2\pi\sigma_c X_c dX_c$$

and changing the order of integration gives,

$$B_c(\sigma_c) = 4 \cdot \int_0^\infty B_o(\sigma_o) \left[\int_0^\infty \cos 2\pi\sigma_o \frac{X_c}{n(\text{HeNe})} \cos 2\pi\sigma_c X_c dX_c \right] d\sigma_o \cdot \tag{11}$$

From the orthogonality of the cosine functions, the Dirac delta function can be written (3):

$$\delta(f-f_o) = 4\int_0^\infty \cos\ [2\pi(f-f_o)\tau]d\tau \tag{12}$$

where

$$\delta(x) = \begin{matrix} 0 \text{ for } x \neq 0 \\ \infty \text{ for } x = 0 \end{matrix}$$

and

$$\int_{-\infty}^{\infty} \delta(x)\ dx = 1.$$

From equation (12), equation (11) can be written:

$$B_c(\sigma_c) = \int_0^\infty B_o(\sigma_o)\ \delta\left(\frac{\sigma_o}{n(\mathrm{HeNe})} - \sigma_c\right)d\sigma_o. \tag{13}$$

Since only the alteration of the wavenumber scale is of interest, inspection of equation (13) shows that the delta function is zero except at,

$$\sigma_c = \frac{\sigma_o}{n(\mathrm{HeNe})} \tag{14}$$

and since the observed wavenumbers are in air, σ_o can be written,

$$\sigma_o = n(\sigma_{Vac}) \cdot \sigma_{Vac} \tag{15}$$

where $n(\sigma_{Vac})$ is the index of refraction of air at the vacuum wavenumber of the spectrum. From equations (14) and (15), the calculated wavenumbers, σ_c, can be related to the vacuum wavenumber of the observed spectrum by,

$$\sigma_c = \frac{n(\sigma_{Vac})}{n(\mathrm{HeNe})} \cdot \sigma_{Vac} \tag{16}$$

The ratio of the indicies of refraction of air in equation (16) is less than one for σ_{Vac} lying in the IR, so the calculated wavenumbers are less than the true (vacuum) wavenumbers. Consider the error, $\Delta\sigma$, resulting from equation (16):

$$\Delta\sigma = \sigma_{Vac} - \sigma_c = \sigma_{Vac}\left(1 - \frac{n(\sigma_{Vac})}{n\ (\mathrm{HeNe})}\right).$$

At room temperature (22°C) and standard pressure (760mm) the error in the calculated wavenumbers at 2000 cm^{-1} is .008 cm^{-1} and at 4000 cm^{-1} the error is .015 cm^{-1}. It is therefore necessary that this error be considered if high precision wavenumber determination is desired. It should be pointed out that the errors described by equations (1) and (16) lead to a lower wavenumber scale than the true scale, thus their effects are additive.

A number of other errors can effect the precision of the wavenumber

scale on the FTS system; however, the errors summarized by equations (1) and (16) are both significant and readily correctable. Problems such as sampling errors, laser instability, and mirror-velocity fluctuations can lead to errors in wavenumber calibration, but these are normally characteristics of a particular FTS system, and may not be easily corrected. While equation (16) can supply a correction to the calculated wavenumber scale by knowing the index of refraction of air, the solid angle in equation (1) can be difficult quantity to accurately measure. One approach to determining the solid angle term in equation (1) is to compare measured line positions with known values. Then, theoretically, the correction term for equation (1) is known for the remainder of the wave number scale. This was the scheme chosen to calibrate the FTS wavenumber scale resulting in a calibration program, FTCAL, which is described in appendix III-1. Using known line positions (up to 100), the solid angle term, $\Omega/4\pi$, in equation (1) is determined by the method of least-squares after altering the known line positions according to equation (16). The reason for altering the known line positions before performing the least-squares calculation is so the only error remaining is that due to equation (1). After the least-squares calculation is performed, corrected values for the measured line positions are computed as follows;

$$\sigma_1 = \frac{\sigma \text{ (measured)}}{1 - \Omega/4\pi}$$

$$\sigma \text{ (corrected)} = \sigma_1 \cdot \frac{n(\text{HeNe})}{n(\sigma_1)} \quad . \tag{17}$$

The corrected values are compared with the (unaltered) known positions to determine the errors between the two sets. If the user has specified an inclusion/rejection criterion (the parameter PR in the program), the errors are compared with the value of PR to determine if a line should be excluded from the least-squares calculation.

If the largest error exceeds PR, the measured line position which yielded that error is excluded from the set of measured values, and the least-squares calculation is repeated. This process is repeated until only the lines yielding an error less than PR are included in the least-squares calculation of $\Omega/4\pi$. If PR is set equal to zero, all lines are included. After a value for $\Omega/4\pi$ is found, unknown lines are read-in and corrected according to equations (17). The index of refraction of air is calculated using Edlen's formula and corrected for non-standard temperature and pressure using ideal gas law corrections [2]. The user of FTCAL must specify the temperature (deg. C) and barometric pressure (mm of Hg) at which the standard lines were measured and the unknown measurements made. It should be pointed out that if the temperature differs by less than ±5°C and the pressure differs by less than ±20 torr between the calibration measurement and the unknown measurement, the error resulting from assuming both were taken under the same conditions is less than .001 cm^{-1} over the wavenumber range 400 cm^{-1} to 4000 cm^{-1}. For a detailed description of FTCAL, the reader is referred to Appendix I.

Another area that needed investigating before making precision line position measurements involved the best methods for determining the line center with the FTS system. Two basic options are available to the FTS user. Firstly, the user may use the intensified cursor to directly read-out the line positions from the c.r.t. display and secondly, the user may read the line position values from a hard-copy plot of the data. The former method is very convenient, but suffers from poor consistency. The latter method is cumbersome and time consuming but yields good measurement consistency. Using the carbon monoxide fundamental as a known set of lines and the overtone as an unknown set (both are known to better than .0002 cm^{-1}) evaluation of the FTS system and the FTCAL program was begun. From these measurements, a

number of guidelines developed. These are summarized below:

1. Dispersive elements (such as lenses) in the collimating optics lead to non-linearities in equation (1) and invalidate that correction if the unknown and known lines differ greatly in wavenumber.

2. Use of the intensified cursor to determine line positions can at best yield a precision of $\pm .005$ cm^{-1}.

3. Use of the plotting routine with the FIT parameter set to YS can lead to a precision of better than $\pm .002$ cm^{-1}. Use of the FIT routine is imperative for good interpolation between data points.

4. Line centers should be determined by using paper with a grid or overlaying plots on a grid. Plots should always be made of absorbance files unless absorbance values are small (<0.1). Plots should be made using a scale factor of 0.1 cm^{-1} per inch or less.

It is felt that a precision of better than $\pm .002$ cm^{-1} is obtainable over the wavenumber range 400 cm^{-1} to 4000 cm^{-1} and perhaps $\pm .001$ cm^{-1} in the wavenumber range below 2000 cm^{-1}.

SECTION II

ROTATIONAL AND VIBRATIONAL POPULATION DISTRIBUTION IN CARBON MONOXIDE

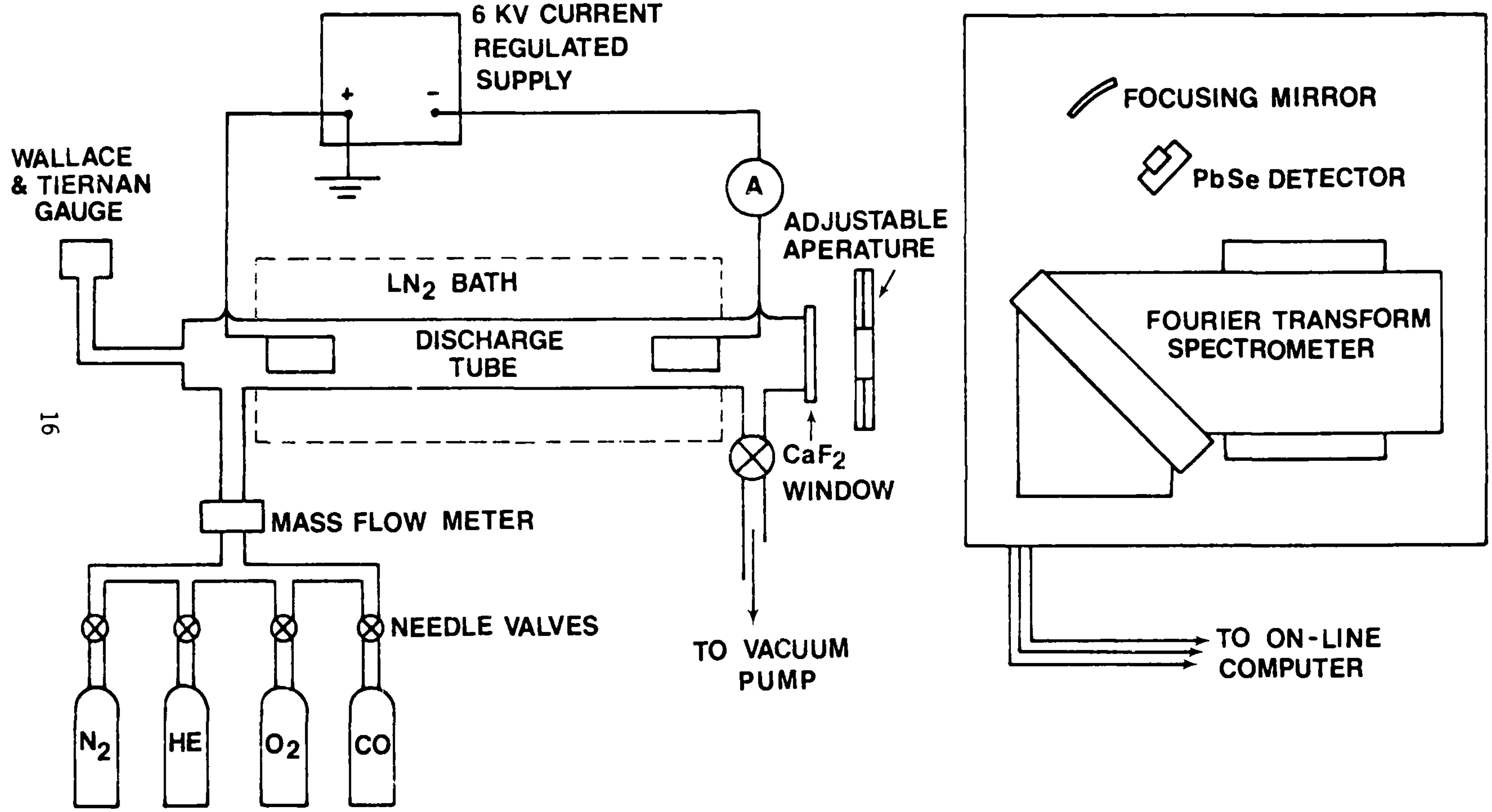
Determination of the rotational temperature and vibrational populations of carbon monoxide in a low pressure gas discharge has been accomplished. A computer code has been developed which allows the user to input low resolution emission data from either the fundamental, first, or second overtone of carbon monoxide and outputs to the user the rotational temperature and the fraction of molecules in each vibrational level. This investigation resulted in a paper being presented at a Mini Symposium on Aerospace Systems Technology - Present and Future, sponsored by the American Institute of Aeronautics and Astronautics.

Figure 4 shows the experimental setup used for making the measurements. Radiation leaving the discharge tube passed through the adjustable aperture, through the fourier transform spectrometer (FTS), and was then focused on the PbSe detector. The discharge tube was a cylinder roughly 2.5 cm. in. diameter and 50 cm. in length. The entire optical path was purged with dry air which was also free of carbon dioxide. Both water vapor and carbon dioxide parasitically absorb the infrared radiation from the discharge. The spectral regions in which these molecules absorb is illustrated in Figure 3, and partially overlaps the emission from CO.

When absorption due to CO_2 and H_2O is not present, the spectrum of the emission from a CO-N_2-He discharge is illustrated in Figure 5. The band at 2000 cm^{-1} is due to many overlapping fundamental transitions $\Delta V=1$ while the band extending from 2800 to 4400 cm^{-1} is due to many overlapping first overtone ($\Delta V=2$) transitions. As shown schematically in Figure 6, each of the overtone transitions has a P and an R branch, but each successive

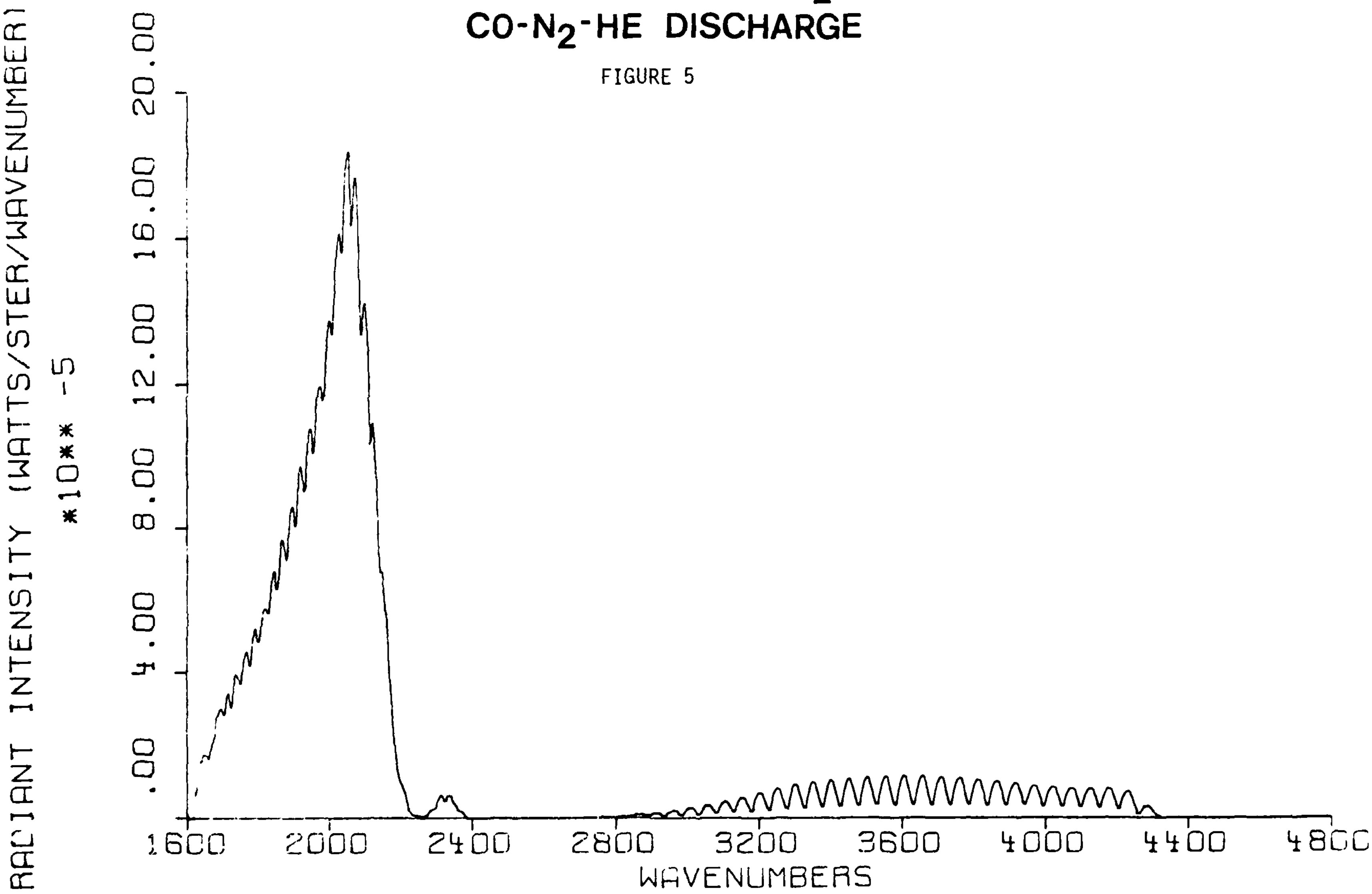
SCHEMATIC OF THE EXPERIMENT

FIGURE 4

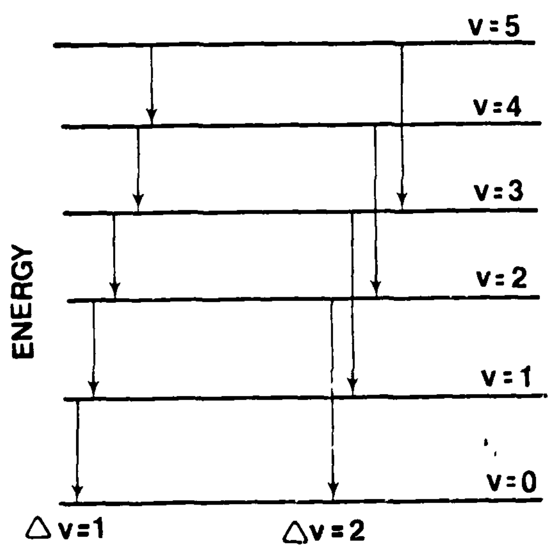


LOW RESOLUTION INFRARED EMISSION SPECTRUM OF A LN_2-COOLED CO-N_2-HE DISCHARGE

FIGURE 5



FUNDAMENTAL (△V=1) AND FIRST OVERTONE (△V=2) VIBRATIONAL TRANSITIONS



OVERLAP OF THE VIBRATIONAL BANDS IN THE FIRST OVERTONE

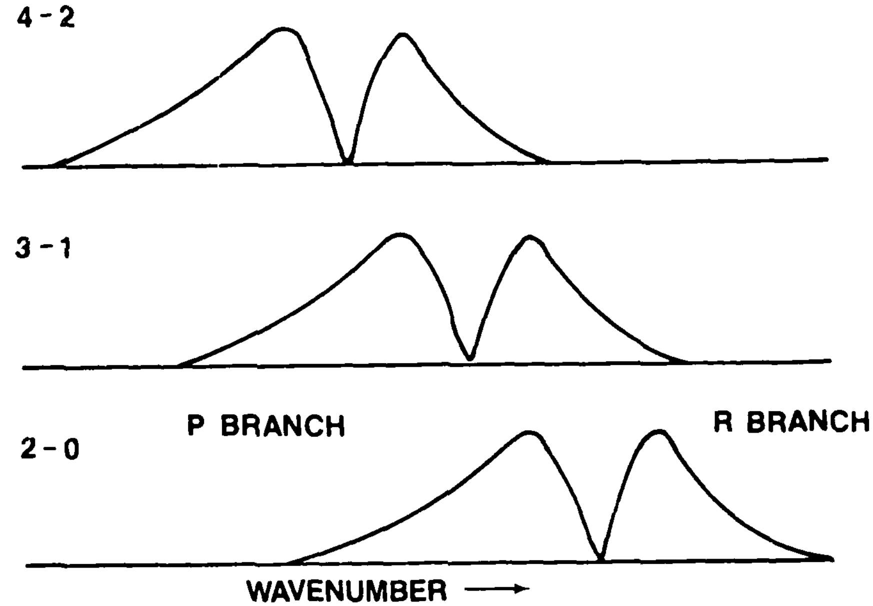


FIGURE 6

transition is shifted to lower wavelength because of vibrational anharmonicity. The observed spectrum is the overlap of many slightly shifted P and R branches. It should be noted in Figure 5 that the R-branch of the V = 2 to V = 0 transition is not overlapped by any other bands, hence the theoretical description of the intensity in this region is greatly simplified. Figure 7 is detailed plot of the CO first overtone emission showing the structure resulting from more than 30 vibrational levels contributing to the spectrum.

The approach taken to the problem of determining the rotational temperature and vibrational populations from data typified in Figure 7 was guided by three primary considerations. First, determine the rotational temperature and vibrational populations that yield a "best fit" between a measured and a theoretical first overtone spectrum. Second, the computation should be efficient and free from "trial and error" fitting procedures. Third, because of the non-equilibrium nature of the problem, no assumption about the behavior of the vibrational populations can be made. In addition, two assumptions made in the approach were that the distribution of molecules among rotational lines could be treated as delta functions.

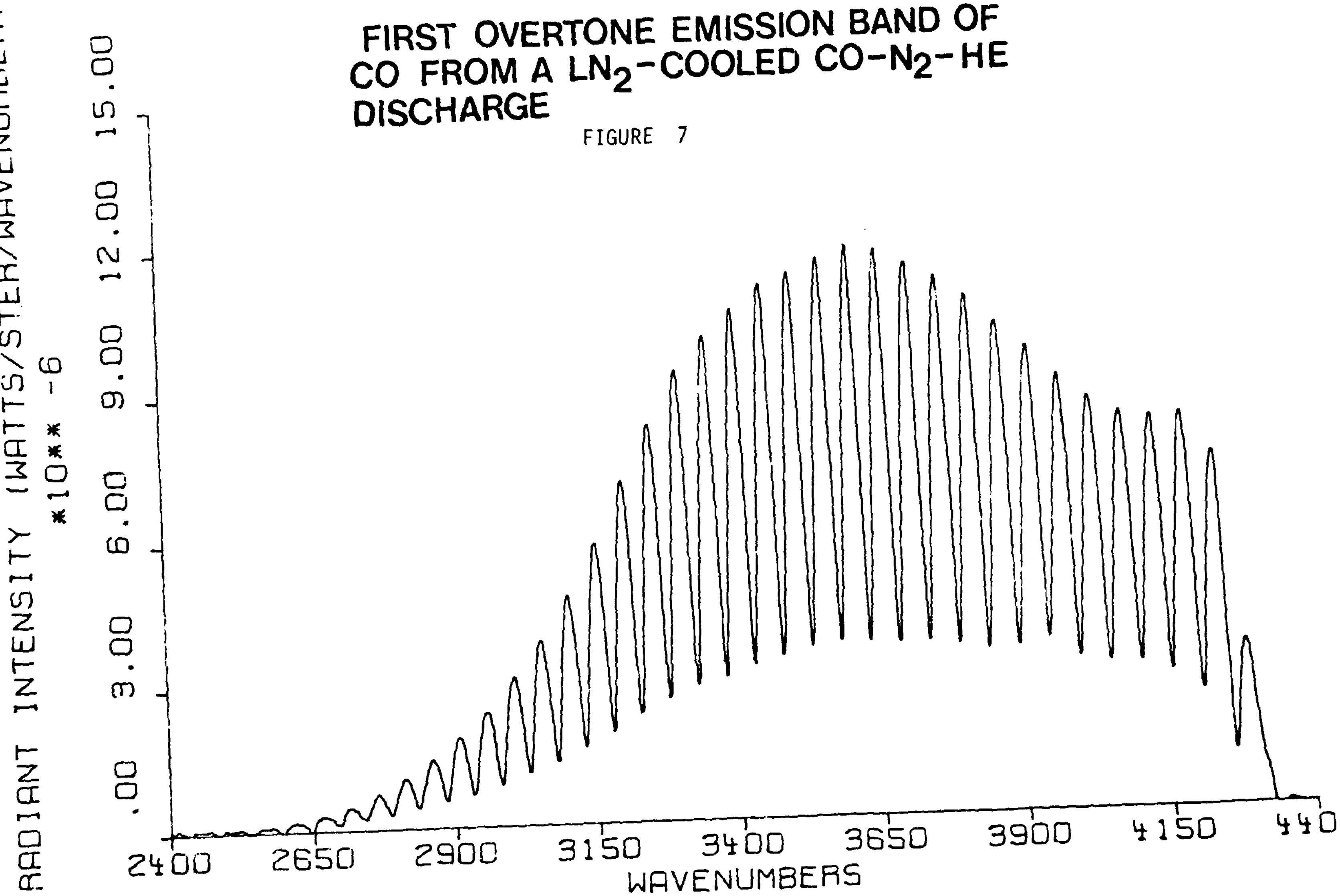
The method of solution developed from this approach is outlined below.

I. Correct the measured spectrum for the instrument response function. The instrument response function (IRF) is found by dividing a measured black body spectrum by the theoretical black body spectrum. Raw spectral data is subsequently corrected by dividing by the IRF. This procedure removes effects due to beamsplitter variations, detector sensitivity, amplifier gain, etc. The spectra shown were corrected in this manner.

II. Calculate the rotational temperature from the R-branch of the 2-0 transition. Because the 2-0 R-branch is not overlapped

FIRST OVERTONE EMISSION BAND OF CO FROM A LN_2-COOLED $CO-N_2-HE$ DISCHARGE

FIGURE 7



by other bands, the shape only depends on T_{ROT} and the V = 2 number density. These parameters are determined by performing a two parameter, non-linear least squares fit between the measured and theoretical 2-0 R-branch.

III. Calculate the vibrational populations using data from full overtone spectrum. Using T_{ROT} from II, a theoretical overtone spectrum is generated which is a function of the number densities in each vibrational level. A multiple linear regression analysis is then used to determine the set of vibrational populations that yield a best fit.

IV. Compare the resulting theoretical spectrum with the measured spectrum. Step I is performed on the FTS data system while the remaining steps are performed on a CDC 6600 by the computer code CODIAG. A listing of this code is Appendix II. Data points are taken from the FTS data system and manually punched on cards for the 6600.

A map of the structure of CODIAG is shown in Figure 8. The first step in the analysis is to determine the rotational temperature from the spectral data of the R-branch of the 2-0 transition. The intensity of the CO emission in this region can be written as,

$$I(\sigma) = N_2 f(\sigma;T_R) \qquad (18)$$

where $I(\sigma)$ is the intensity at wavenumber σ, N_2 is the number of CO molecules in the v=2 level, and $f(\sigma;T_R)$ is a function which is non-linear in the rotational temperature, T_R. The behavior of the function $f(\sigma;T_R)$ is the result of the intensity distribution among the rotational lines of the 2-0 R-branch folded with the spectrometer instrument function. The unknown parameters N_2 and T_R in equation (18) are determined from a set of measured

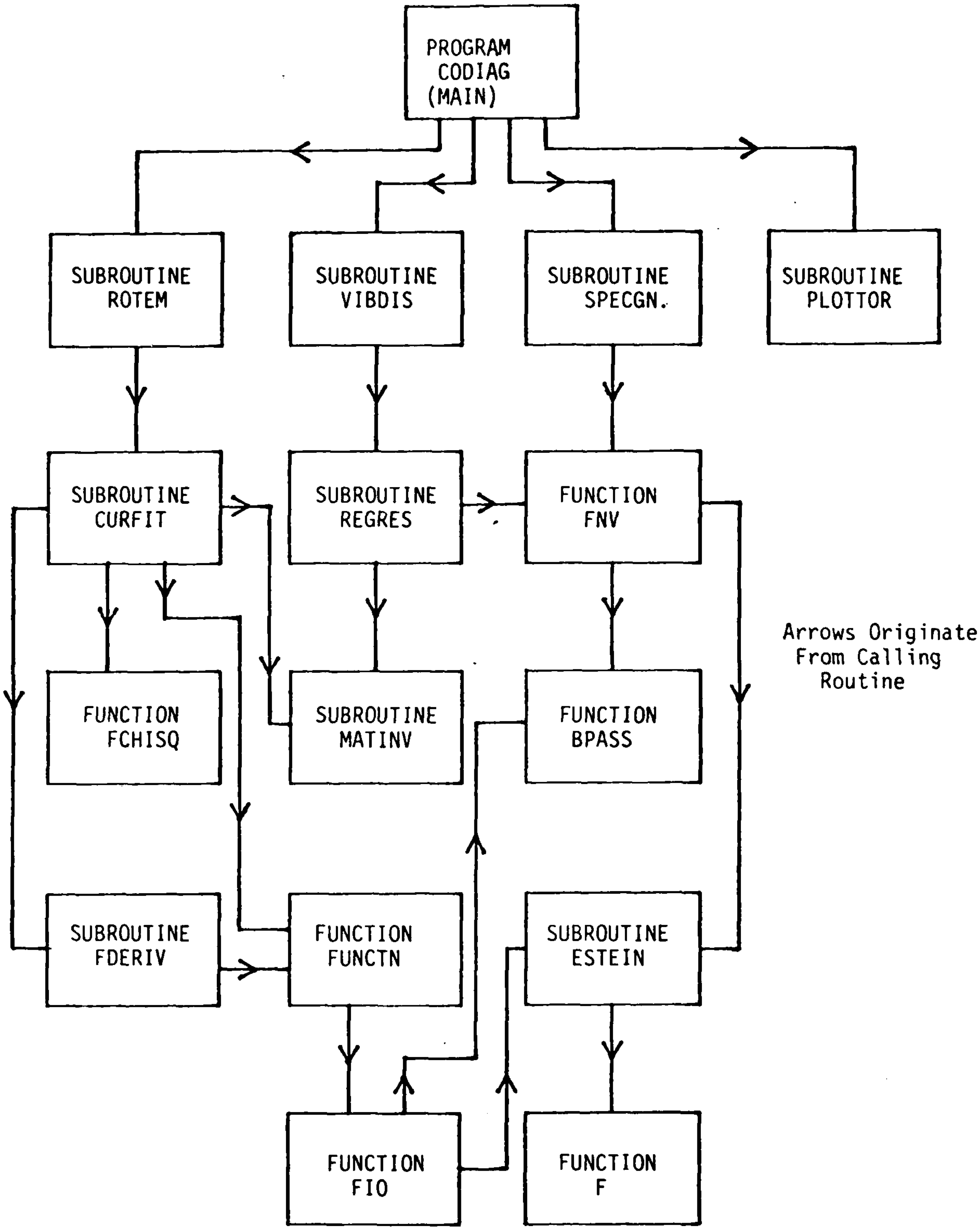


FIGURE 8 PROGRAM STRUCTURE OF CODIAG

intensities $\{I(\sigma_i)\}$ using the non-linear least-squares fitting procedure developed by Marquardt [4] and described in Bevington [5]. The technique is iterative and requires initial guesses for N_j and T_R. This procedure is applied through the CODIAG SUBROUTINE ROTEM. Initial guesses and data input is through ROTEM while the actual least-squares algorithm is contained in SUBROUTINE CURFIT which is modified version of a program appearing in Bevington [5]. The right side of equation (18) is calculated in FUNCTION FIO which is called by CURFIT through the intermediary FUNCTION.

The intensity at any point in the calculated spectrum can be written

$$I(\sigma_i) = \sum_{j=2}^{n} N_j f_j(\sigma_i;T_R) \tag{19}$$

where N_j is the number of molecules in the j^{th} vibrational level and $f_j(\sigma_i;T_R)$ includes the behavior of the rotational intensity distribution folded with the spectrometer instrument function. Since T_R has already been found, write $f_j(\sigma_i;T_R)$ as $f_j(\sigma_i) \equiv f_{ji}$. Then equation (19) becomes

$$I(\sigma_i) = I_i = \sum_j N_j f_{ji} \quad . \tag{20}$$

Since the measured intensities might contain a zero offset, the function used to describe the measured spectrum is written

$$I_i = \alpha_o + \sum_j N_j f_{ji} \quad . \tag{21}$$

It is desired then to find the set $\{N_j\}$ from a measured set of intensities $\{Y_i\}$. The method chosen for this is to minimize the function χ^2 by adjusting the set $\{N_j\}$. χ^2 is given by

$$\chi^2 = \sum_i \frac{1}{\Delta_i{}^2} (Y_i - I_i)^2 \tag{22}$$

where Δ_i is the standard deviation of the i^{th} measured intensity. At the minimum of χ^2, the partial derivatives of χ^2 with respect to α_o and each parameter N_j are zero or

$$\frac{\partial \chi^2}{\partial \alpha_o} = \frac{\partial \chi^2}{\partial N_2} = \cdots\cdots = \frac{\partial \chi^2}{\partial N_n} = 0 \tag{23}$$

Substitute equation (21) into equation (22) and apply condition (23) yields a set of linear equations which can be solved for α_o and the set $\{N_j\}$. The reader is refered to Bevington [5] for a detailed description of the solution. Tha application of this scheme to determine the set $\{N_j\}$ is through SUBROUTINE VIBDIS (See Figure 8). The actual multiple linear regression is performed in SUBROUTINE REGRES which is a modified version of a program appearing in Bevington [5]. The functions f_{ji} in equation (21) are calculated in FUNCTION FNV. In addition to handling the data I.O. from the vibrational population determination, VIBDIS also calculates values for N_o and N_1 from an assumed Treanor distribution 6 over the lower vibrational level. The Treanor distribution can be written as

$$N_v = N_o . \mathrm{Exp}\ (V\Theta - E_v/kT) \tag{24}$$

where E_v is the energy of the V^{th} vibrational level compared to the V=0 energy, Θ is a constant at a fixed gas temperature, k is the Boltzmann constant, and T is the kinetic (and rotational) temperature of the gas. The value of Θ can be determined from equation (24) with the previously determined values of N_2 and N_3 and is given by

$$\Theta = \ln\left(\frac{N_3}{N_2}\right) + (E_3 - E_2)/kT \tag{25}$$

Using equation (25) and equation (24), along with the calculated values for N_2 and N_3 , the Treanor values for N_0 and N_1 can be found.

As an initial test of CODIAG, data points were taken from a synthetic spectrum generated from a known T_R and a known set $\{N_j\}$ and input into CODIAG. This test would indicate if the program could determine T_R and the set $\{N_j\}$ from a limited number of data points. The results for a 30 level set $\{N_j\}$ were excellent. A more difficult test was to determine the desired parameters from a measured spectrum. Data was obtained from a liquid nitrogen cooled CO-N_2-He discharge with a 1:2:10 mixture ratio and operating at a pressure of about 1 torr. The discharge length was about 50 cm and the current and voltage were 15 mA at 4.9 Kv. In addition, about .15% of the total pressure was oxygen. The measured overtone spectrum is shown in Figure as obtained with a Fourier Transform Spectrometer with a resolution of about $10cm^{-1}$. Calibration of the system was achieved by comparing a theoretical 700°K black body function with a measured spectrum from a standard source. Eighteen data points were taken from the R-branch of the 2-0 transition for the determination of T_R and an additional seventy four data points were taken throughout the spectrum for determination of the vibrational populations. The data points chosen were primarily the "peaks" and "valleys" of the vibrational structure in the spectrum. The rotational temperature was found to be 207°K with an estimated uncertainty of $\pm$10°K. The calculated vibrational population distribution is illustrated in Figure 9, which is a plot of the log of the relative occupation number versus vibrational level. The relative occupation number is given by $N_j/\Sigma N_j$.

Also shown in Figure 9 is the population distribution from a room temperature discharge shown in Figure 10. The stars correspond to the data in Figure 7 and the rectangles correspond to the data in

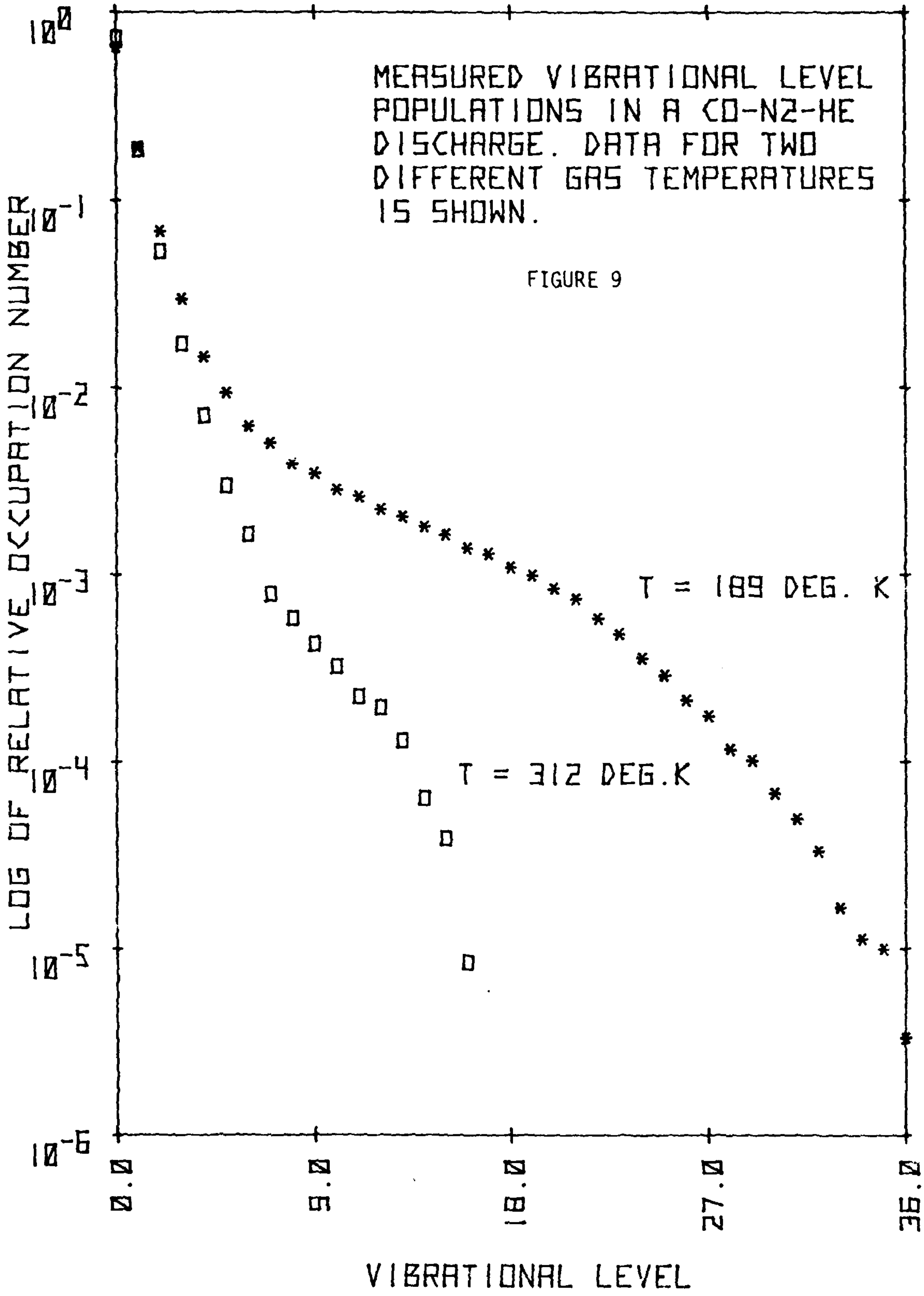
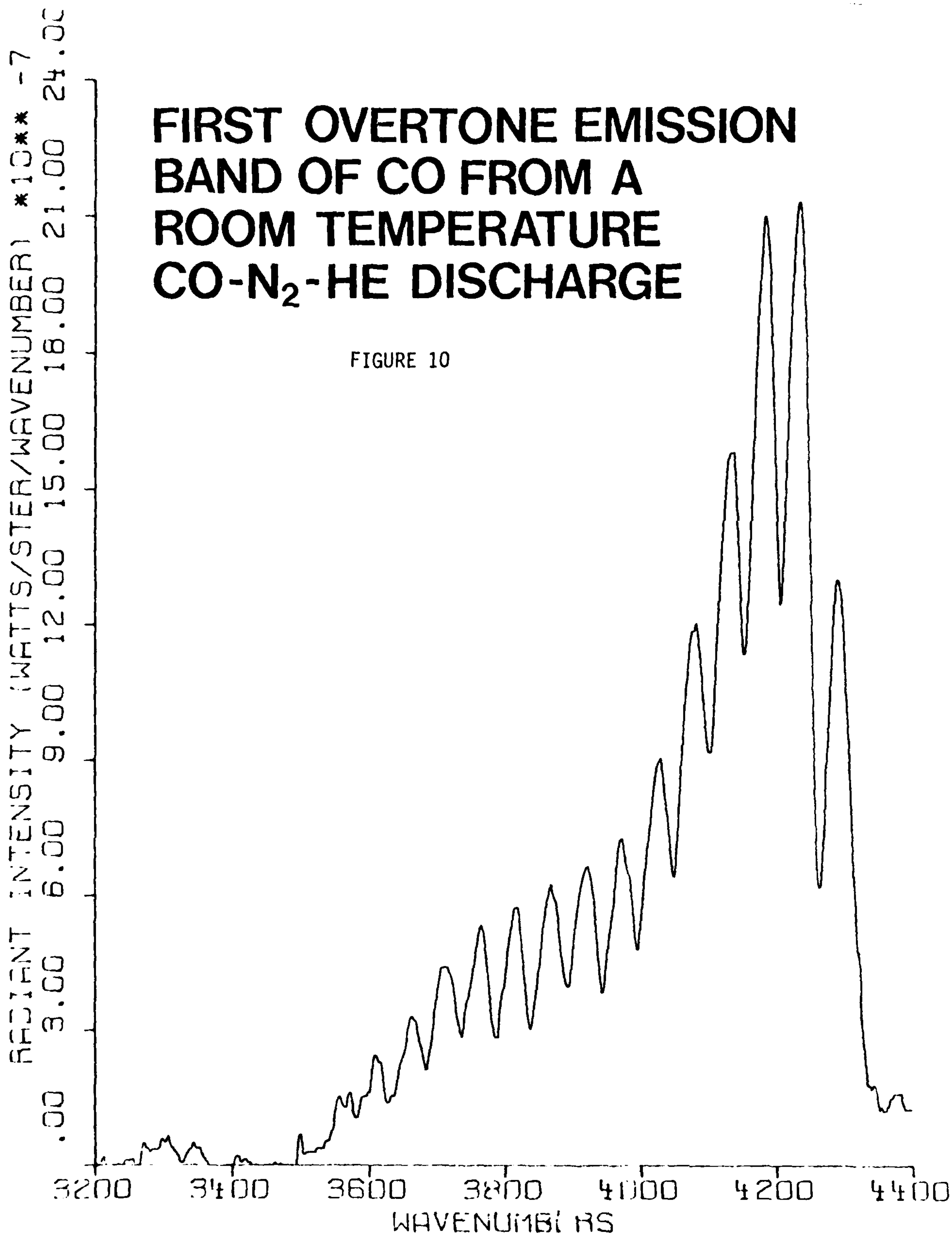

MEASURED VIBRATIONAL LEVEL
POPULATIONS IN A CO-N2-HE
DISCHARGE. DATA FOR TWO
DIFFERENT GAS TEMPERATURES
IS SHOWN.
T = 189 DEG. K
T = 312 DEG.K
LOG OF RELATIVE OCCUPATION NUMBER
10^0
10^-1
10^-2
10^-3
10^-4
10^-5
10^-6
0.0
9.0
18.0
27.0
36.0
VIBRATIONAL LEVEL

FIGURE 9

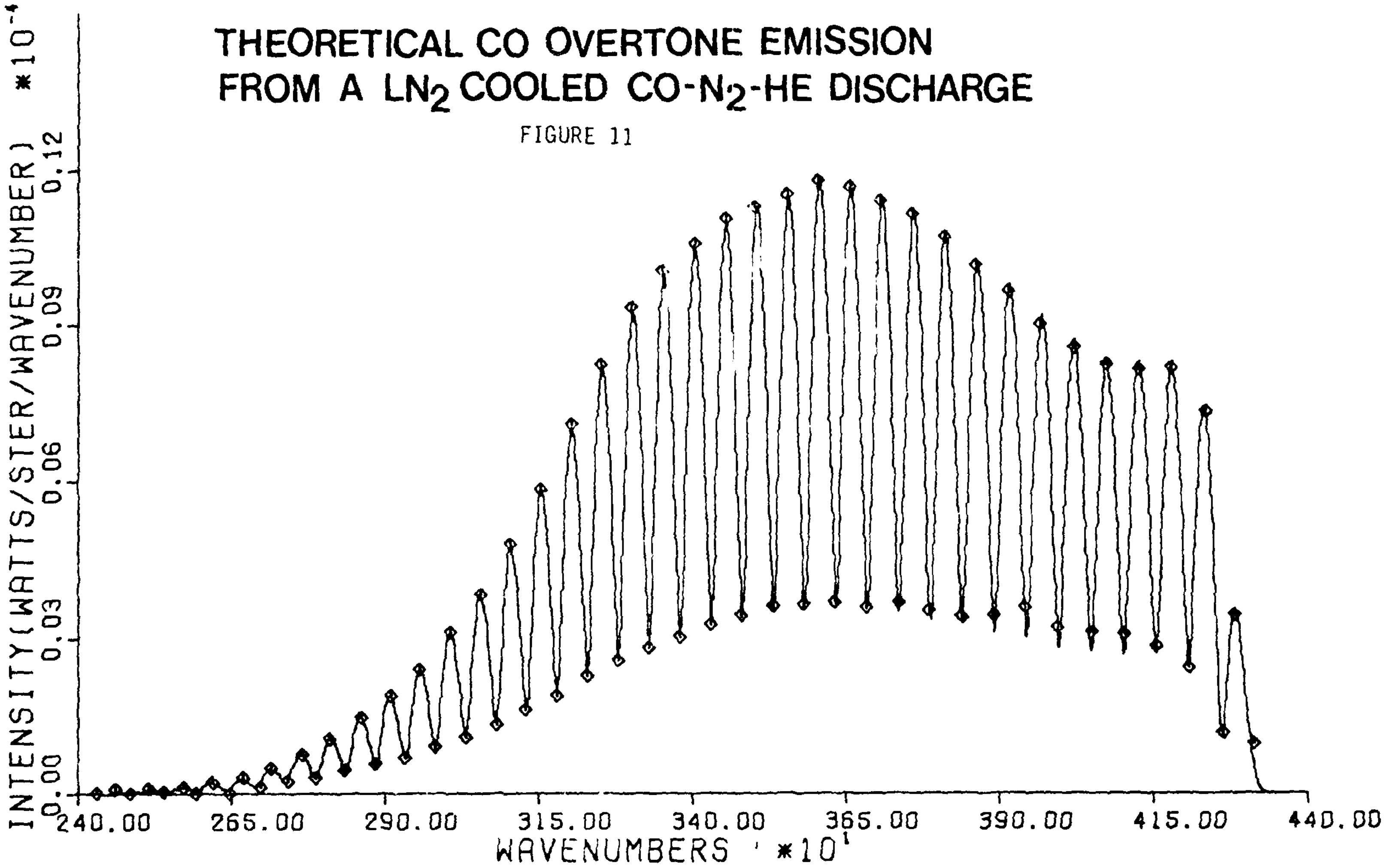


FIRST OVERTONE EMISSION BAND OF CO FROM A ROOM TEMPERATURE CO-N_2-HE DISCHARGE

FIGURE 10

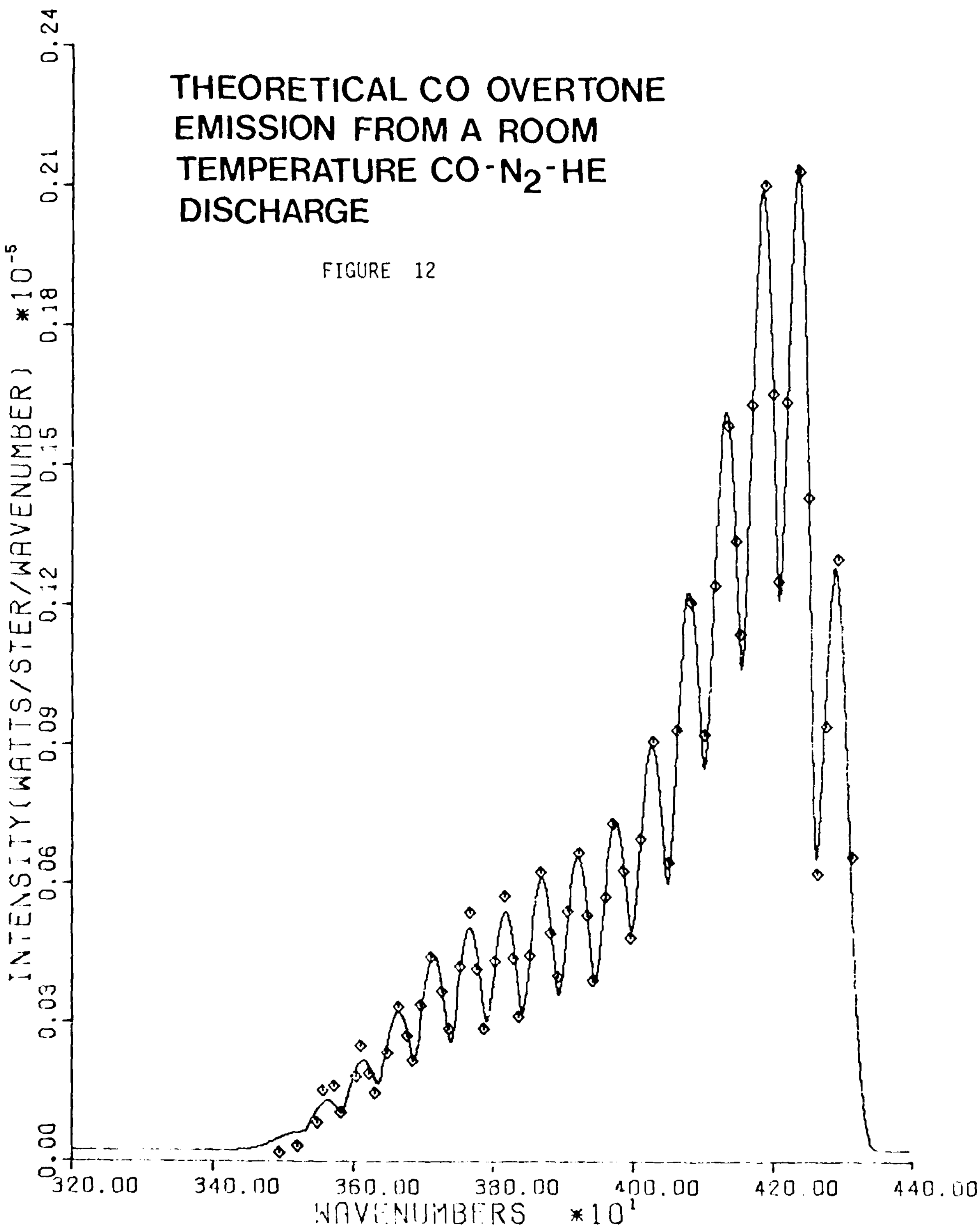
Figure 10. The theoretical spectra calculated from these vibrational populations and rotational temperature are shown in Figure 11 and Figure 12. In these figures, the small diamonds indicate the data points used in the analysis. Figure 11 and Figure 12 can be compared with Figure 7 and Figure 10 as an indication of the confidence in the results shown in Figure 9.

From the results shown here, some conclusions can be drawn as to the limitation of the diagnostics along with some guidelines for determining its sensitivity. With a signal-to-noise ratio (S/N) on the order of 100, vibrational population data has been calculated over 5 orders of magnitude. With a S/N on the order of 65 in the 2-0 R-branch, the estimated standard deviation in T_{ROT} is less than 5% of T_{ROT}. It appears that a good estimate of the relationship between S/N in the R-branch and the standard deviation in T_{ROT} is given by $(\Delta T/T) \cdot (S/N) \simeq 1.3$. The chief sources of error in the calculation of the vibrational populations are probably systematic. Errors in correcting for system sensitivity and errors in calculating the CO transition probabilities are probably large compared to the fluctuations in the vibrational populations due to a S/N greater than 20. Measurement times can be shortened, down to the time required for a single scan of the FTS, with a corresponding decrease in S/N. Single scan times can be less than 0.1 sec. with an effective noise equivalent power of $\simeq 7 \times 10^{-10}$ watt/cm^{-1} at 4000 cm^{-1}. This effective NEP includes detector noise plus electronic noise and is adjusted for the system response function. Hence, if the radiant intensity of a source is known and the solid angle subtended at the FTS detector, this effective NEP can be used to give an estimate of the single scan S/N that can be expected. Inherent in the FTS technique is the need for sources to subtend a small solid angle



THEORETICAL CO OVERTONE EMISSION FROM A LN_2 COOLED $CO\text{-}N_2\text{-}HE$ DISCHARGE

FIGURE 11


THEORETICAL CO OVERTONE EMISSION FROM A ROOM TEMPERATURE CO-N2-HE DISCHARGE
FIGURE 12
INTENSITY(WATTS/STER/WAVENUMBER) *10^-5
0.00
0.03
0.06
0.09
0.12
0.15
0.18
0.21
0.24
320.00
340.00
360.00
380.00
400.00
420.00
440.00
WAVENUMBERS *10^1

at the detector; however, for low resolution this requirement is not as stringent as needed for high resolution. For the resolution needed in this analysis, the source may subtend a solid angle as large as 6×10^{-3} ster. without degrading the technique. Lastly, it should be pointed out that absorption by water vapor in the optical path would completely prohibit obtaining vibrational population data; however, T_{ROT} is still measureable because the 2-0 R-branch lies outside the water vapor band.

SECTION III

ABSORPTION BY DISCHARGE IMPURITIES

A number of gas mixes which model the gas found in the electron beam closed cycle discharge were studied in an effort to determine detection sensitivities for a number of minor species.

The first trace species studied were N_2O, NO, and NO_2. These were chosen for their strong absorption bands in the PbSe region and their suspected presence in CO_2 laser discharges. Gas mixes of 3 parts N_2, 1 part CO_2 and various concentrations of the nitrogen oxides were made up and their absorption spectra obtained. Total pressure in the White cell was kept at 200 torr. This was done for the following reasons. First, below one half atmosphere the line widths of the trace species are on the order of the best spectral resolution obtainable with the FTS System (.06 cm^{-1}). Thus, below $\approx$ 380 torr, the observed line widths should be pressure independent and interference between neighboring lines will be at a minimum. Second, the ratio of the volumes of the available sample cylinders to the White cell volume is about 1:5, so with an EBCC pressure of 1 atm., the White cell pressure should be on the order of 150 torr. Running the gas mixes at 200 torr was a reasonably good approximation to the conditions under which samples were to be studied.

With the gas mix just discussed, N_2O shows two reasonably strong absorption bands that are free from interfering species. The bands originate from the $00^01 \rightarrow 00^00$ and $20^00 \rightarrow 00^00$ transitions and are centered at 2223.8 cm^{-1} and 2563.3 cm^{-1} respectively [7]. Figure 13 shows a portion of the P-branch of the $00^01 \rightarrow 00^00$ band while Figure 14 shows both branches of the $20^00 \rightarrow 00^00$ band. These spectra were obtained with 100 ppm N_2O

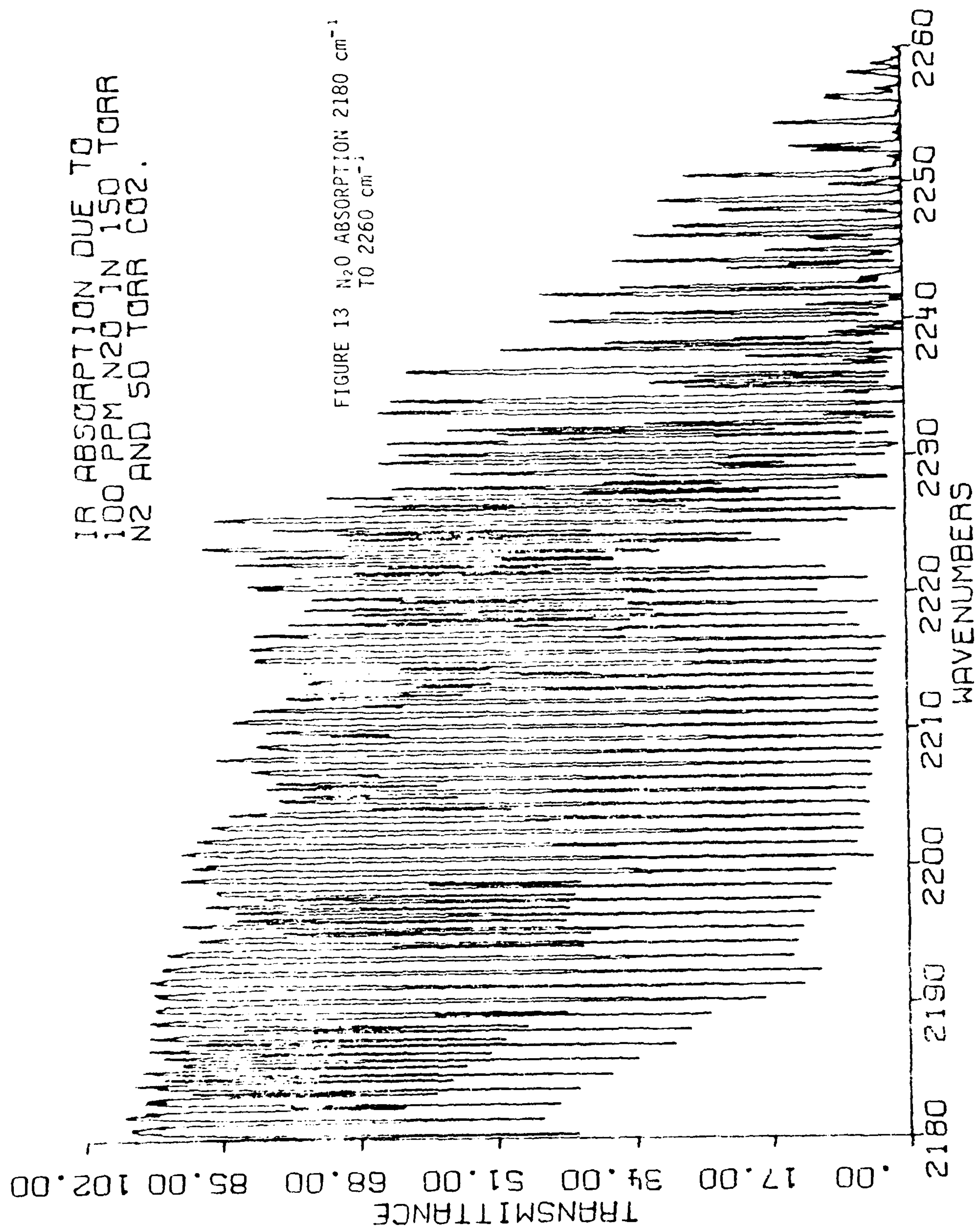


FIGURE 13 N_2O ABSORPTION 2180 cm^{-1} TO 2260 cm^{-1}

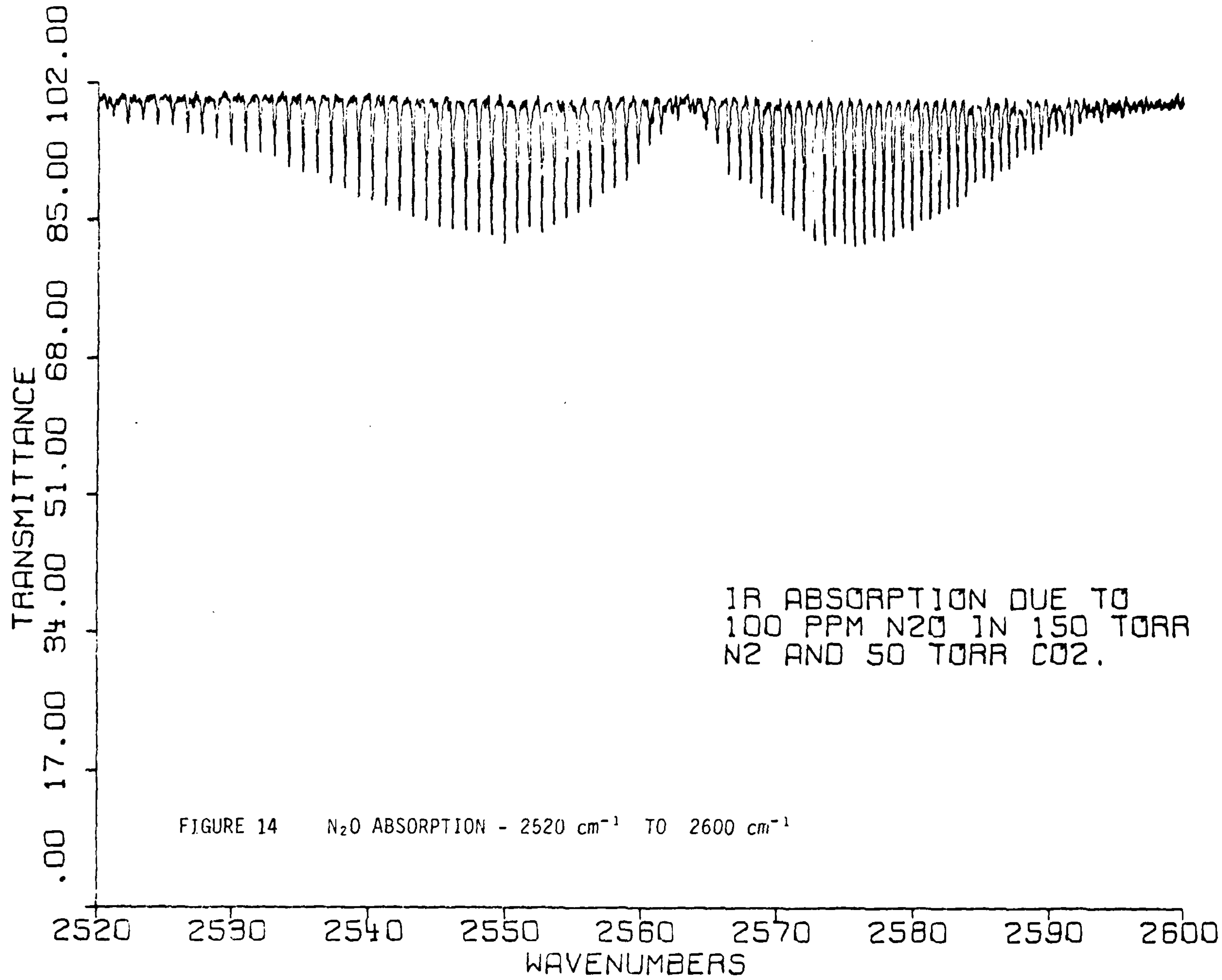


FIGURE 14 N_2O ABSORPTION - 2520 cm^{-1} TO 2600 cm^{-1}

in the 3:1 N_2:CO_2 gas mix previously discussed. The P-branch of the $00^01 \rightarrow 00^00$ transition lies at the edge of strong absorption by a number of CO_2 bands; thus there is some interference with the lower J-value N_2O lines. The R-branch of the $00^01 \rightarrow 00^00$ transition is completely obscured by the CO_2 absorption. Figure 15 shows the same spectral region as Figure 13 only the N_2O is missing from the gas mix and the CO pressure is somewhat higher. It can be seen that above about 2200 cm^{-1} interference from CO_2 prohibits the used of the N_2O lines for determining its presence. The $20^00 \rightarrow 00^00$ band lies in an interference-free region, but lacks the strong absorption of the $00^01 \rightarrow 00^00$ band. Table 1 is a summary of the results for the two N_2O bands along with expected band strengths for the two bands studied. Lines are chosen based on the criteria of being relatively interference-free and showing strong absorption. The effective absorption coefficient was calculated from the slope of the straight line found by a least squares fit of concentration dependence of absorption. Errors were calculated assuming a 1% error in the transmission measurements which was roughly the noise level of 2000 sec. run with the PbSe detector. The transmission through the gas is given by:

$$I = I_0 e^{-\alpha p} \qquad (26)$$

where (in this case), α is in units of $torr^{-1}$ and hence p is the partial pressure in torr. The estimated detection limit for each band shown in Table 1 is found by assuming a value of I/I_0 of .995 can be measured (with the new InSb detector), and finding the pressure that yields this value. The estimate is good at a total pressure of 200 torr and changes with total pressure. Below about on half atmosphere, the detection limit is expected

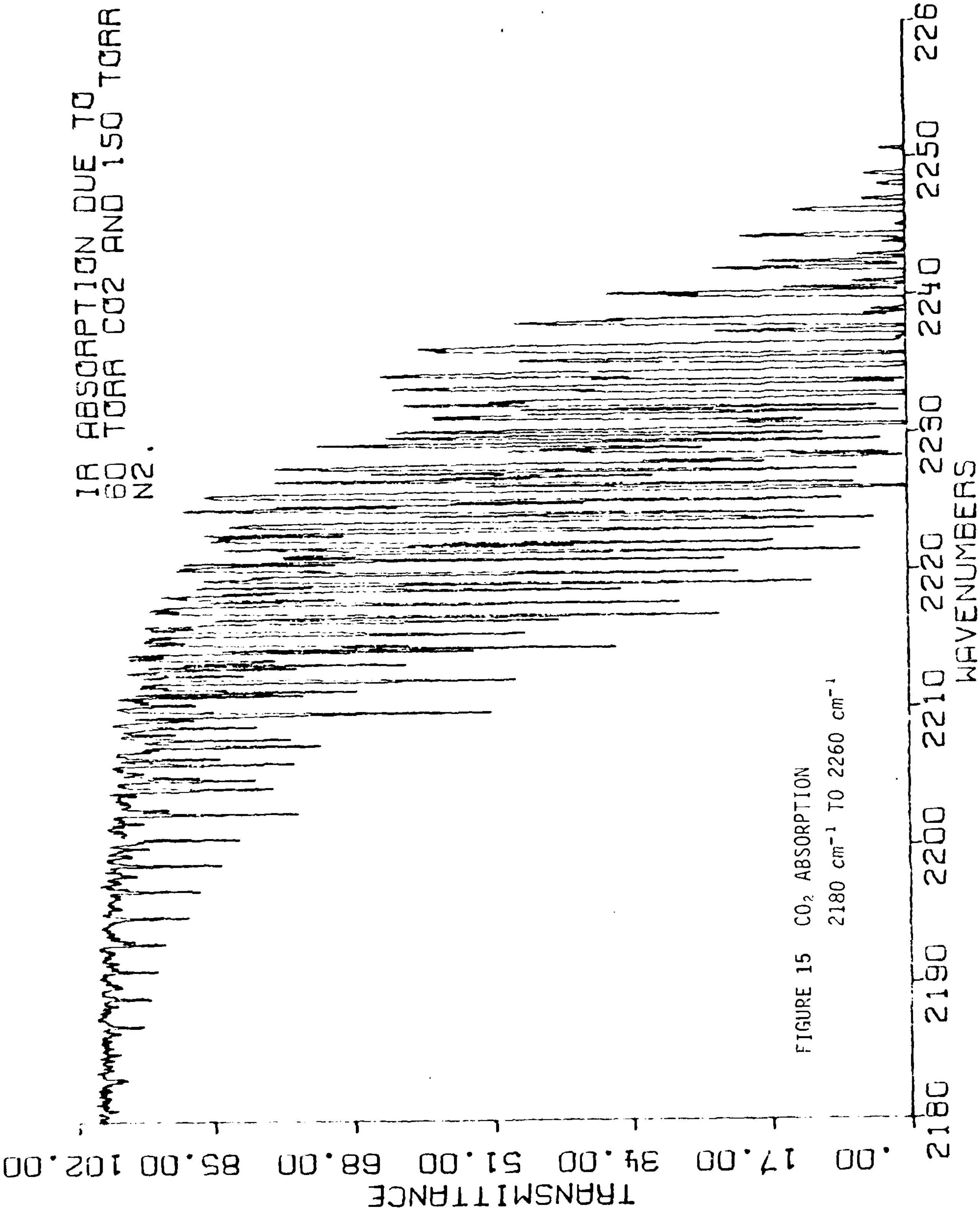


FIGURE 15 CO_2 ABSORPTION
$2180\ cm^{-1}$ TO $2260\ cm^{-1}$

TABLE 1

ABSORPTION DATA FOR NITROUS OXIDE

Band (Ref. 7)	Band Strength (Ref. 7) $cm^{-1}/cm\text{-}atm$	Line Identification (Ref. 8)	Line Position (Ref. 8)	Measured Effective Absorption Coefficient ($Torr^{-1}$)	Estimated Detection Limit (At 200 Torr Total Pressure)	Interferring Species
$00^01 \rightarrow 00^00$	1536 ± 67	P(37)	2188.1898	58.99 ± 1.37	≃ .4 ppm	CO (Strongly Inteferring) CO_2
		P(36)	2189.2734	63.97 ± 1.50		
		P(35)	2190.3502	79.58 ± 1.96		
		P(34)	2191.4203	102.7 ± 2.8		
		P(33)	2192.4837	113.7 ± 3.2		
$20^00 \rightarrow 00^00$	36.3 ± 1.9	P(17)	2548.1716	9.47 ± .85	≃ 2.5 ppm	None
		P(16)	2549.1178	9.98 ± .85		
		P(15)	2550.0573	10.04 ± .86		
		P(14)	2550.9901	9.59 ± .85		
		P(13)	2551.9162	9.17 ± .84		
		P(12)	2552.8355	9.08 ± .84		
		R(12)	2573.6132	10.17 ± .86	≃ 2.5 ppm	None
		R(13)	2574.3556	9.10 ± .86		
		R(14)	2575.0912	9.88 ± .86		
		R(15)	2575.8199	10.51 ± .86		
		R(16)	2576.5418	9.75 ± .86		
		R(17)	2577.2569	9.78 ± .86		

to increase linearly with decreasing total pressure while above one-half atmosphere the detection limit should be roughly constant due to pressure broadening. For example, for the $00^01 \rightarrow 00^00$ band the minimum detectable amount of N_2O at 100 torr total pressure would be roughly twice the value given while at atmospheric pressure the value would be somewhat less that the given value.

The fundamental band of nitric oxide, entered near 1876 cm^{-1}, lies in a region of strong water vapor absorption. While the P-branch lies in the stronger part of the H_2O band, the R-branch is over-lapped by the $11^10(2) \rightarrow 00^00$ band of CO_2 [7] (the number in parenthesis locates the level in the Fermi resonating group). Due to the high number densities of CO_2 in this experiment, it was decided to use lines of the P-branch that were not too strongly overlapped by H_2O lines. Table 2 gives the results of the measurements on NO and Figure 16 shows a typical absorption spectrum of the selected NO lines. The numbers arrived at in Table 2 were found in the same manner as in the N_2O data with one exception. The estimated detection limit was based on being able to measure a transmittance of 99% as opposed to 99.5% for the N_2O data. This was done because of the poorer signal-to-noise level in the 1800 cm^{-1} region of the InSb detector.

The strongest NO_2 band in the IR is the ν_3 band centered at 1362.03 cm^{-1} [Ref. 9]. An average of the bandstrength measurements for this band yield a value [9] of 848 cm^{-1}/cm-atm. which is somewhat larger than one half the N_2O ν_3 bandstrength. The difficulty in using this band for detecting NO_2 is that it lies in the middle of a very strong water vapor band which blocks most of the NO_2 signal. Figure 17 shows the water vapor absorption in this region as a result of the spectrometer operating in laboratory air. The

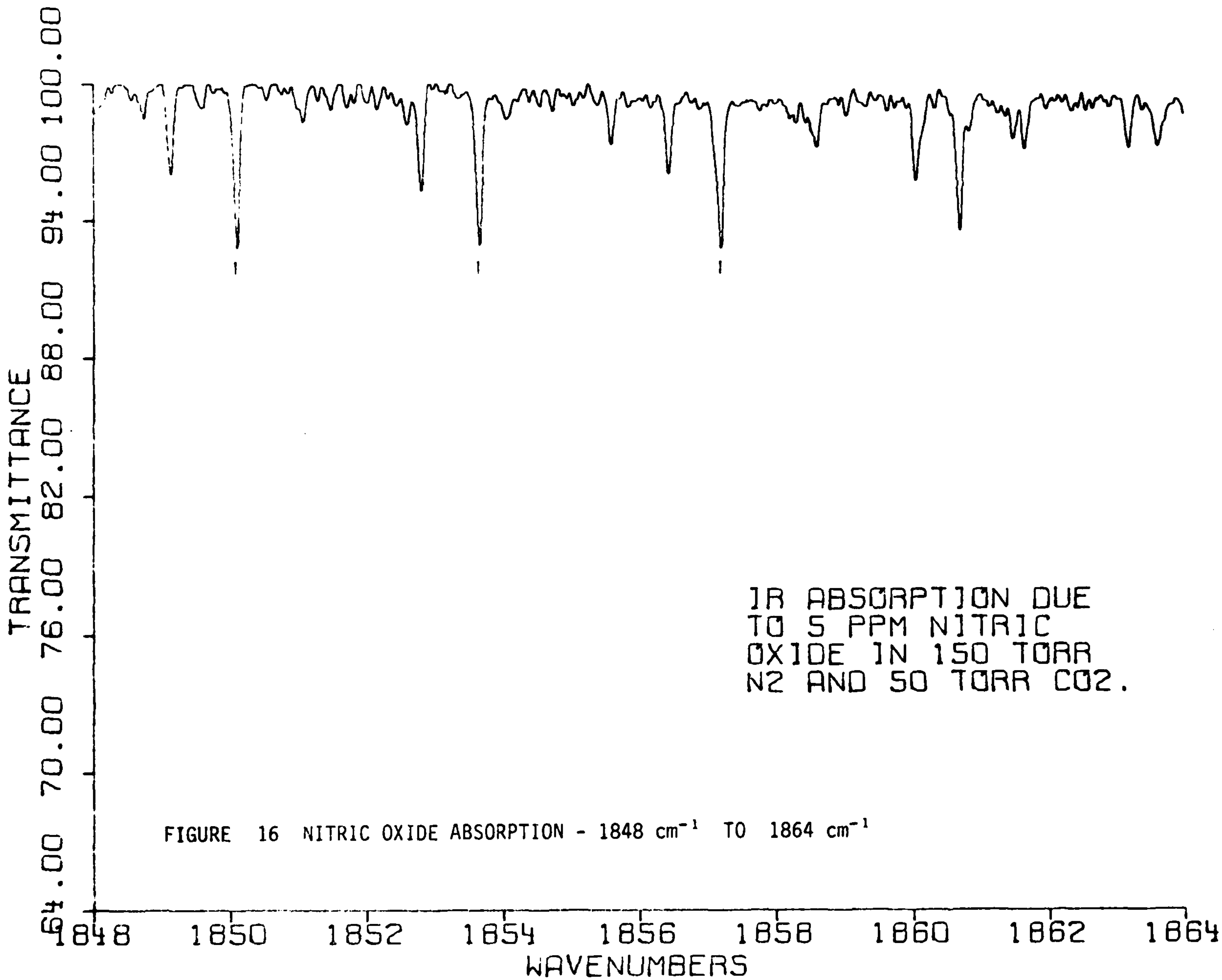


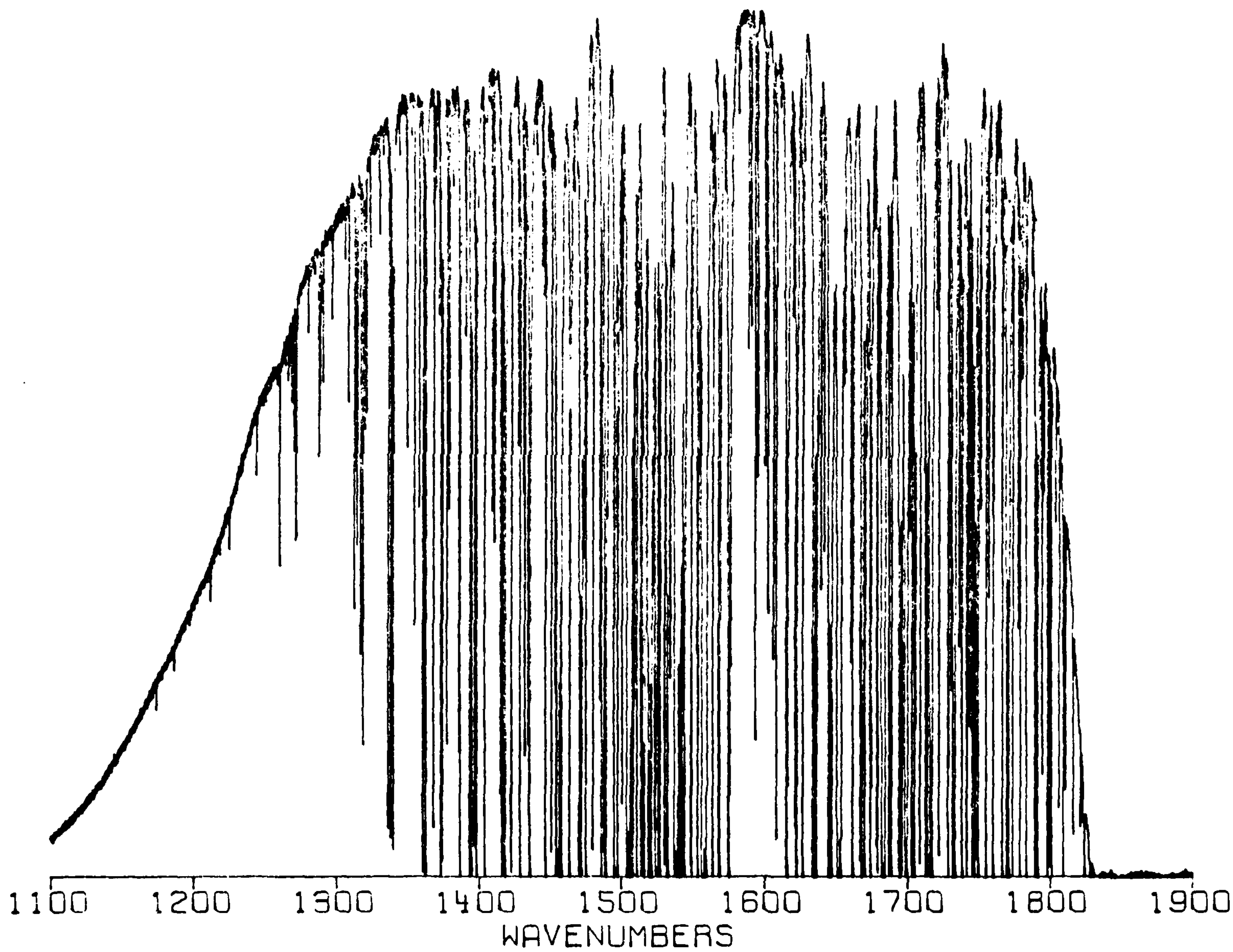
FIGURE 16 NITRIC OXIDE ABSORPTION - 1848 cm^{-1} TO 1864 cm^{-1}

TABLE 2

ABSORPTION DATA FOR NITRIC OXIDE

Band (Ref. 9)	Band Strength (Ref. 9) $cm^{-1}/cm\text{-}atm$	Line Identification (Ref.10)	Line Position (Ref. 10)	Measured Effective Absorption Coefficient ($Torr^{-1}$)	Estimated Detection Limit (At 200 Torr Total Pressure)	Inteferring Species
1 - 0	128	P(15/2)	1850.1757	39.88 ± 1.95	≈ 1.3 ppm	H_2O
$^2\pi_{1/2}$		P(13/2)	1853.7417	36.86 1.88		CO_2
		P(11/2)	1857.2736	37.07 1.85		

FIGURE 17 WATER VAPOR ABSORPTION - 1100 cm^{-1} TO 1850 cm^{-1}



spectrum was obtained using the HgCdTe half of the "sandwich" detector and the interferometer fitted with the Fe_2O_3-CaF_2 beamsplitter. The cutoff of signal near 1100 cm^{-1} is due to the CaF_2 transmission while the cutoff near 1850 cm^{-1} is due to the transmission through the InSb part of the "sandwich". From Figure 17, it is clear that it will be difficult to observe NO_2 absorption in this region; however, there is a small "window" in the water vapor centered at 1586 cm^{-1} which is shown in Figure 18. Figure 19 shows the absorption in this region due to 50 ppm NO_2 in 150 torr N_2 and indicates that it should be possible to use this region to detect NO_2. An alternative band which could be used is the $\nu_1 + \nu_3$ band of NO_2 centered near 2906 cm^{-1}. This band is free of interfering species; however, the band strength is only 17 cm^{-1}/cm-atm (average of measurements [10]) and hence will yield a higher detection limit.

Since the CO spectrum is well known, only mention of the interference free lines will be given here. In the fundamental band, the P(3), P(2), P(1), and R(0) lines were selected for being free from interference by either CO_2 or N_2O lines while in the first overtone, all lines were considered essentially interference free.

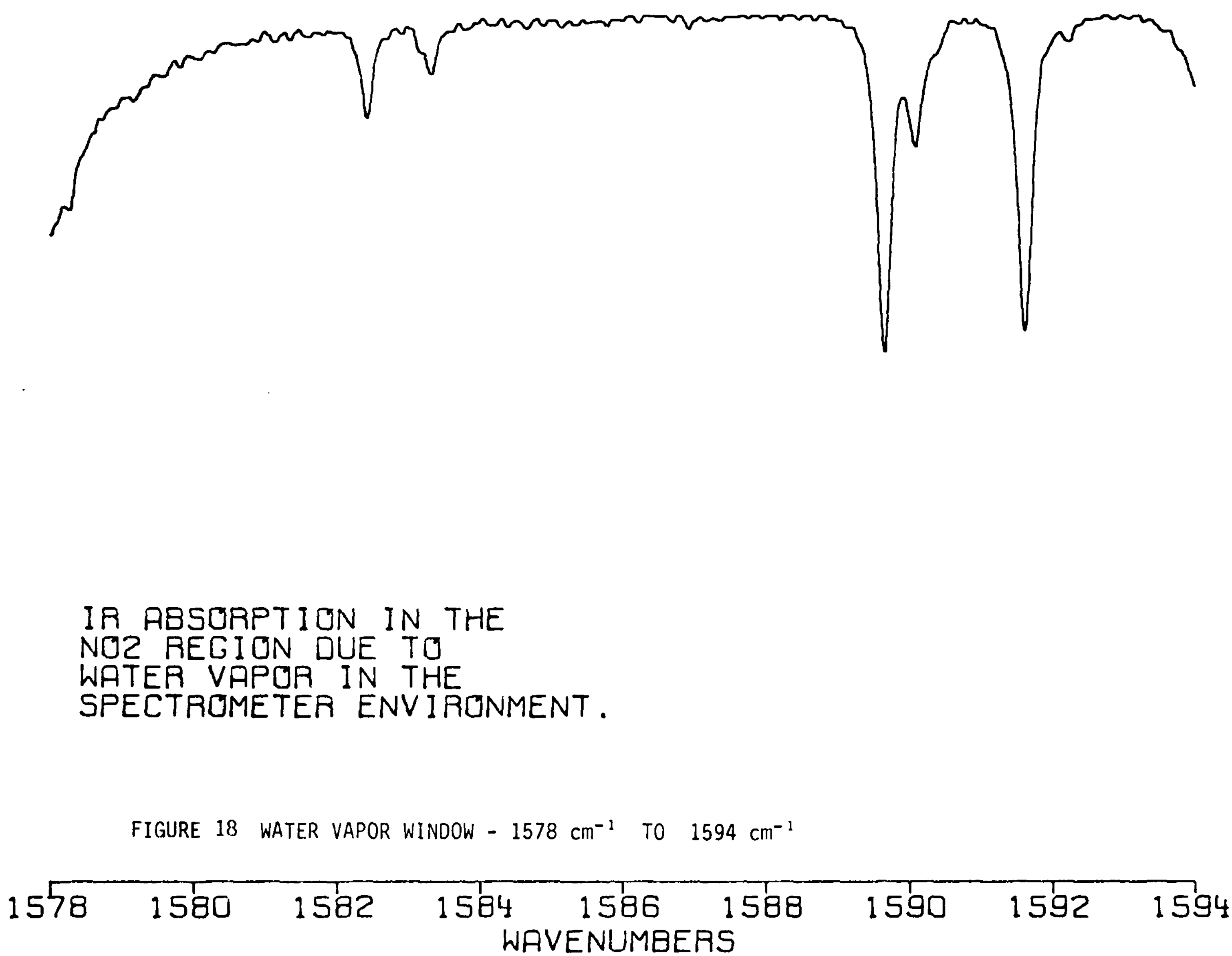


FIGURE 18 WATER VAPOR WINDOW - 1578 cm^{-1} TO 1594 cm^{-1}

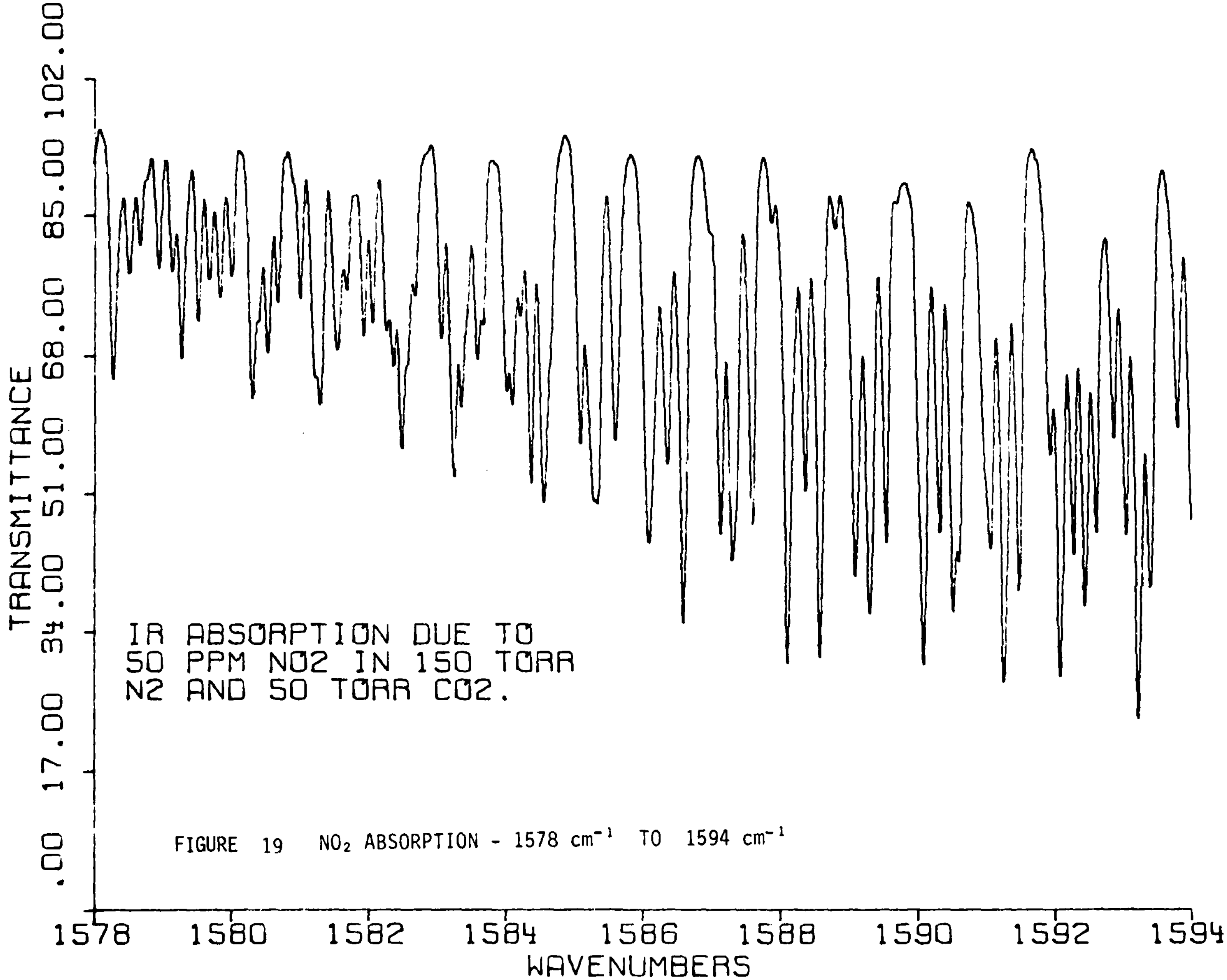


FIGURE 19 NO_2 ABSORPTION - 1578 cm^{-1} TO 1594 cm^{-1}

SECTION IV

CALIBRATION PROCEDURE FOR IMPURITY CONCENTRATION

The easiest measured quantity that can be related to the partial pressure of a particular species is the transmittance of the gas at one of the absorbing wavelengths. If radiation from a source passes through the gas, the transmittance of the gas can be written

$$T(\nu) = 100\% \times \frac{I(\nu)}{I_0(\nu)} \tag{27}$$

where $I(\nu)$ is the intensity of the radiation reaching the detector after passing through the gas, and $I_0(\nu)$ is the intensity of the radiation reaching the detector when no gas is present. Theoretically, this can be related to the partial pressure of the absorber by

$$T(\nu) = 100\% \times \int_{-\infty}^{\infty} F(\nu-\nu') \cdot \exp\left\{-p \cdot x \cdot k(\nu')\right\} d\nu' \cdot \tag{28}$$

In equation (28), p is the partial pressure of the absorber, x is the path-length over which the absorption occurs, $k(\nu')$ is the absorption coefficient for the particular species as a function of wavenumber (or wavelength), and $F(\nu-\nu')$ is the spectrometer bandpass function, normalized according to

$$\int_{-\infty}^{\infty} F(\nu) d\nu = 1. \tag{29}$$

If the spectrometer bandpass function is much "narrower" than the width of a spectral line, $F(\nu-\nu')$ in equation (28) goes over to a delta function and the measured transmittance is just

$$T(\nu) = 100\% \times \exp\left\{-p \cdot x \cdot k(\nu)\right\} \cdot \tag{30}$$

In this case, if one knows the absorption coefficient and the pathlength, the partial pressure can be calculated directly.

Unfortunately, the situation that exists when samples are analyzed with the White cell-FTS system is not so simple. The gas samples are normally at pressures of 100 torr or less which results in spectral linewidths on the order of 0.01 cm^{-1} (FWHM) or less, while the best instrument resolution is on or order of 0.06 cm^{-1}. Under these conditions the functional dependence of the transmittance on the partial pressure of the species becomes more complex. The simplest approach to solving this problem is to use calibration curves to relate the measured transmittance to the partial pressure of the species. In this procedure, a series of spectra are taken of gas mixes which contain known amounts of the species of interest and a calibration curve is constructed for each absorption line of each species. Then for a particular absorption line, one can write

$$T_k = A_k(p) \tag{31}$$

where the index k is used to indicate a particular line and A_k is the particular function that describes the transmittance of that line. This was the procedure initially chosen for calibration of the White-cell FTS system. The difficulty with using the aforementioned calibration procedure lies in the dependence of the function A_k on the other system parameters. For example, if the resolution of the spectrometer is changed, a new set of A_k's must be generated for each new resolution setting. More important however, A_k is strongly dependent on the background gas pressure and weakly dependent on the composition of the background gas. Thus a separate set of calibration curves would have to be constructed for each total pressure run in the EBCC system or in the TEA laser experiment,

and for each gas mix chosen. For an experiment such as the EBCC system or the TEA laser, where one would like to vary these parameters at will, producing calibration data becomes exceedingly time consuming. An alternate calibration procedure, though perhaps less accurate, is to work directly with equation (28) to interpolate and extrapolate a manageable amount of calibration data. This has been the procedure adopted for the White cell-FTS system.

To see how equation (28) depends on the background pressure and gas mix, one needs to consider the absorption coefficient $k(\nu)$. For an isolated spectral line, $k(\nu)$ can be written [11]

$$k(\nu) = \frac{S}{\alpha_D} \left(\frac{\ln 2}{\pi}\right)^{\frac{1}{2}} V(w,y) \tag{32}$$

where $V(w,y)$ is the Voigt function given by

$$V(w,y) = \frac{y}{\pi} \int_{-\infty}^{\infty} \frac{\exp(-t^2)dt}{y^2 + (w-t)^2} . \tag{33}$$

In equation (32), S is the integrated line strength and α_D is the Doppler half-width of the line given by

$$\alpha_D = \nu_0 \left(\frac{2kT \ln 2}{Mc^2}\right)^{\frac{1}{2}} \tag{34}$$

where ν_0 is the wavenumber of the line, k is Boltzmann's constant, T is the gas temperature in Kelvin. M is the mass of the molecule, and c is the speed of light. In equations (32) and (33), w and y are defined by

$$w = \frac{\nu - \nu_c}{\alpha_D} (\ln 2)^{\frac{1}{2}} \tag{35}$$

and

$$y = \frac{\alpha_L}{\alpha_D} \quad (36)$$

where ν is the wavenumber at which $k(\nu)$ is desired, ν_0 and α_D are as before, and α_L is the Lorentz half-width of the line. The Lorentz width is made up of two components, the natural width α_N and the collision width α_C. For the range of pressures studied here, $\alpha_N << \alpha_C$ so that for purposes of this study $\alpha_L = \alpha_C$. The collision half-width of the line is given by

$$\alpha_C = \sum_i \gamma_i p_i \quad (37)$$

where γ_i is the line broadening coefficient for the line under study, broadened by the i^{th} component in the gas mixture and p_i is the partial pressure of the i^{th} component. From equation (37) it can be seen that the collision half-width, and hence the absorption coefficient $k(\nu)$, depend on the total pressure of the gas and the particular species present. To use equation (28) to calculate partial pressures one must therefore know the line strength S of the particular line, the molecular weight of the absorbing species, and the broadening coefficients for each major species present in the gas mix. In addition, the partial pressures of the major components of the gas mix must also be known.

Since most of the data mentioned in the previous paragraph could be obtained from the open literature, one possible calibration scheme would consist of gathering the existing data and calculating the partial pressures of the major species directly. Since it was desired to develop a calibration scheme consistent with the calibration data that had already been obtained, a somewhat different scheme was chosen. It was found in the calculations that errors in the assumed widths of the lines were of less importance than errors in the individual line strengths. In addition, measurement

of broadening coefficients would require many additional calibration measurements which would be quite time consuming. So for these reasons, the calibration scheme chosen involved using broadening coefficients from the open literature along with line strengths calculated from the calibration data. Before any of this could be implemented, a number of computer codes had to be developed in order to evaluate equation (28). To calculate the Voigt function in equation (32) a code due to Armstrong [11] was modified slightly and implemented. This function subprogram is called VOIGT. To evaluate equation (28) a code called FOLD1 was written which uses Simpson's one-third rule to evaluate the integral. The step size in FOLD1 is automatically adjusted to handle variations in line width and the limits on the integral are adjusted in accordance with the instrument resolution. The spectrometer bandpass function is supplied by a function subprogram called BPASS1 which was written especially for this FTS system. To calculate the strength of a particular line it was necessary to "solve" equation (28) for S (from equation (32)) given a particular line center transmittance, partial pressure, and line width. For this, a code called SEEKER2 was written which solves equation (28) for S by an iterative procedure. Finally, after the line strengths were estimated a code was needed to solve equation (28) for p given $k(\nu_0)$ and $T(\nu_0)$ for an "unknown" gas sample. A code called SEEKER1 was written for this purpose and like SEEKER2 uses an iterative approach. Data arrived at for use in measuring minor species in the White cell FTS system is presented in Tables 3 through 7. The lines in the tables were primarily selected because they are free from interference by strong water vapor lines, hot bands of CO_2, and lines of other minor species. Whenever possible, two bands of the same molecule were used (weak and strong) to increase the dynamic range of the measurement and further reduce the chances of interference. The line strengths given in the third column of each table were arrived at by

TABLE 3

LINE PARAMETERS FOR SELECTED INTERFERENCE-FREE LINES OF THE $^{12}C^{16}O$ FUNDAMENTAL

Line Designation	Line Position[a] (cm^{-1})	Line Strength (cm^{-2} atm^{-1} @296°)		Line Broadening Coefficients (cm^{-1} atm^{-1})			
		This Work[b]	Literature Value[c]	Self[d]	CO_2[e]	N_2[d]	He[d]
P(3)	2131.6320	--	5.888	.0785	.0967	.0721	.0466
P(2)	2135.5466	--	4.158	.0831	.1026	.0776	.0468
P(1)	2139.4265	--	2.161	.0877	.1118	.0812	.0479
R(0)	2147.0816	--	2.209	.0877	.1118	.0812	.0479

NOTES FOR TABLE 3

a. From Reference 1
b. For the CO Fundamental, it was felt that the literature values were far superior to any that could be measured in this experiment
c. Calculated from data of Reference 12. Uncertainty is probably less than ±5%
d. From Reference 13
e. From Reference 14

TABLE 4

LINE PARAMETERS FOR SELECTED LINES OF THE $^{12}C^{16}O$ 1st OVERTONE

Line Designation	Line Position[a] (cm^{-1})	Line Strength (cm^{-2} atm^{-1} @296°)		Line Broadening Coefficients (cm^{-1} atm^{-1})			
		This Work[b]	Literature Value[c]	Self[d]	CO_2[d]	N_2[d]	He[e]
P(8)	4227.3544	6.758E-02	6.832E-02	.0682	.0782	.0635	.0455
P(7)	4231.6853	6.904E-02	6.984E-02	.0695	.0813	.0630	.0455
P(6)	4235.9474	6.781E-02	6.859E-02	.0711	.0848	.0652	.0458
R(6)	4285.0093	8.506E-02	8.604E-02	.0695	.0813	.0640	.0455
R(7)	4288.2901	8.578E-02	8.673E-02	.0682	.0782	.0635	.0455
R(8)	4291.4998	8.359E-02	8.455E-02	.0670	.0755	.0630	.0455

NOTES FOR TABLE 4

a. From Reference 1
b. Estimated uncertainty is ±5%. Bandstrength calculated is 2.27 ± .11 cm^{-2} atm^{-1} at 300°K
c. Relative strengths calculated from Reference 12, but scaled to yield band strength used in Reference 15 ie. 2.291 cm^{-2} atm^{-1} at 300°K. Uncertainty is probably less than 5%
d. From Reference 14
e. From Reference 13

TABLE 5

LINE PARAMETERS FOR SELECTED INTERFERENCE FREE LINES OF THE $^{14}N^{16}O$ FUNDAMENTAL

Line Designation	Line Position[a] (cm^{-1})	Line Strength (cm^{-2} atm^{-1} @296°)		Line Broadening Coefficients (cm^{-1} atm^{-1})			
		This Work[b]	Literature Value[c]	Self[d]	CO_2[e]	N_2[f]	He[e]
($^2\pi_{1/2}$)							
P(15/2)	1850.1757	2.684	2.53	.0589	.0683	.0589	.0405
P(13/2)	1853.7417	2.624	2.47	.0583	.0676	.0583	.0401
P(11/2)	1857.2736	2.468	2.32	.0595	.0690	.0595	.0409
P(9/2)	1860.7713	2.205	2.07	.0611	.0709	.0611	.0420

NOTES FOR TABLE 5

a. From Reference 10
b. Estimated uncertainty is ±2.4%. Bandstrength calculated is 127 ± 3 cm^{-2} atm^{-1} at 300°K
c. From Reference 16 Bandstrength given is 122 ± 6 cm^{-2} atm^{-1} at 300°K (an uncertainty of approx. ±5%)
d. From Reference 16 (average value of $^2\pi_{1/2}$ and $^2\pi_{3/2}$ states)
e. J dependence is assumed to be the same as Reference 16, but absolute value results from multiplying γ (self) values from Reference 16 by $\gamma(x)/\gamma(\mathrm{self})$ from Reference 8
f. Assumed to be the same as γ (self) from Reference 16

TABLE 6

LINE PARAMETERS FOR SELECTED INTERFERENCE-FREE LINES OF THE ν_3 BAND OF $^{14}N_2\,^{16}O$

Line Designation	Line Position[a] (cm^{-1})	Line Strength (cm^{-2} atm^{-1} @ 296°)		Line Broadening Coefficients (cm^{-1} atm^{-1})			
		This Work[b]	Literature Value[c]	Self[d]	CO_2[e]	N_2[f]	He[g]
P(37)	2188.1898	5.192	5.07	.0713	.0673	.0681	.0508
P(36)	2189.2734	5.873	5.73	.0720	.0666	.0680	.0507
P(35)	2190.3502	6.610	6.45	.0728	.0659	.0679	.0506

NOTES FOR TABLE 6

a. From Reference 8
b. Estimated uncertainty is ±10%. Calculated bandstrength is 1190 ± 107 cm^{-2} atm^{-1} at 300°K
c. From Reference 18. Uncertainty given is about ±2.6%. Bandstrength is 1173 ± 30 cm^{-2} atm^{-1} at 300°K
d. The J-dependence of Reference 19 was used but values were normalized so that P(35) coefficient agreed with that of Reference 20. Reference 20 value is corrected for temperature dependence by $(296/300)^{\frac{1}{2}}$
e. The J-dependence of Reference 19 was used but values were normalized to the $|m|=6$ value of Reference 21 for $\gamma(CO_2)$ at J=6
f. The values from Reference 19 were multiplied by 0.9 to bring them in line with the data from Reference 21 and 22
g. Same as note e except values were normalized to the γ(He) value of Reference 21

TABLE 7

LINE PARAMETERS FOR SELECTED INTERFERENCE-FREE LINES OF THE $2\nu_1$ BAND OF $^{14}N_2\,^{16}O$

Line Designation[a]	Line Position[b] (cm^{-1})	Line Strength ($cm^{-2}\ atm^{-1}$ @296°)		Line Broadening Coefficients ($cm^{-1}\ atm^{-1}$)			
		This Work[c]	Literature Value[d]	Self[e]	CO_2[f]	N_2[g]	He[h]
P(16)	2549.1178	.5742	.5566	.0933	.0860	.0756	.0563
P(15)	2550.0573	.5745	.5569	.0941	.0860	.0770	.0573
P(14)	2550.9901	.5700	.5700	.5526	.0950	.0860	.0573
R(14)	2575.0912	.6107	.5920	.0941	.0860	.0762	.0568
R(15)	2575.8199	.6128	.5941	.0933	.0860	.0756	.0563
R(16)	2576.5418	.6100	.5914	.0926	.0860	.0749	.0553

NOTES FOR TABLE 7

a. For brevity, only data for six strongest lines is presented here. Data also exists for P(17), P(13), P(12), R(12), R(13), and R(17)
b. From Reference 8
c. Estimated uncertainty is ±5%. Calculated bandstrength is $30.3 \pm 1.5\ cm^{-2}\ atm^{-1}$ at 300°K
d. Relative strengths are from Reference 23. Bandstrength is from Table 14 of Reference 7. Bandstrength is $29.4 \pm 1.5\ cm^{-2}\ atm^{-1}$ at 300°K
e. From Reference 20 scaled to 296° by $(296/300)^{1/2}$
f. J-dependence of Reference 20 with the values normalized to the $|m|=6$ value for $\gamma(CO_2)$ of Reference 21.
g. See Note f of Table III-6
h. See Note g of Table III-6

first taking the averages of the strengths calculated from each calibration curve by SEEKER2, then "smoothing" the values to fit theoretical relative intensities at 296°K. This "smoothing" was done by first calculating a band strength from each line strength using theoretical relative intensities. Then an average band strength and its standard deviation were calculated and a set of line strength derived from this average band strength using the theoretical relative intensities. These final line strengths were taken as the "smoothed" values. The data in Tables 3 through 7 is now on computer cards and used by a driving program called TRACER. TRACER uses SEEKER1 and specific line parameter data to arrive at partial pressures of CO, N_2O, and/or NO in a given sample of gas. A listing of TRACER is given in Appendix III.

SECTION V

IMPURITIES IN CO_2 LASER DISCHARGES

Gas samples from the electron beam closed cycle laser and from a TEA laser were analyzed to determine the extent of dissociation and gas chemical effects in the discharge. Before discussing the results in general, the results from two gas samples will be discussed in detail.

Gas samples from the EBCC loop were always taken before and after running the E-beam to insure that the gas was initially clean. Following irradiation, the samples were introduced into the absorption cell and their spectra taken. Changes in the gas were then noted by comparing the spectra of the pre-irradiated gas with the irradiated sample. The first irradiated sample of gas was from approximately a two hour E-beam run, while the second irradiated sample was taken after about a seven hour run. In both cases, the pre-irradiated samples showed only the spectra expected from the 1:2:3 mix. For the two hour irradiated sample, the only difference from the pre-irradiated gas was the presence of CO lines in the irradiated sample spectrum. The seven hour irradiated sample, however, showed significant changes. For example, Figure 20 shows a portion of the absorption spectrum of the pre-irradiated gas while Figure 21 shows the same region of the spectrum of the irradiated sample. In the irradiated sample spectrum both N_2O and CO lines can be clearly seen in addition to the CO_2 lines from the 1:2:3 mix. Figure 22 shows a calibration spectrum of 38 ppm N_2O in the 1:2:3 mix and indicates the order of magnitude of the N_2O absorption. In addition to the N_2O lines and the CO lines, lines due to NO were also seen in the irradiated sample which were not seen in the pre-irradiated gas. Figure 23 shows a portion of the irradiated sample spectrum showing the NO lines, while Figure 24 shows a typical calibration spectrum.

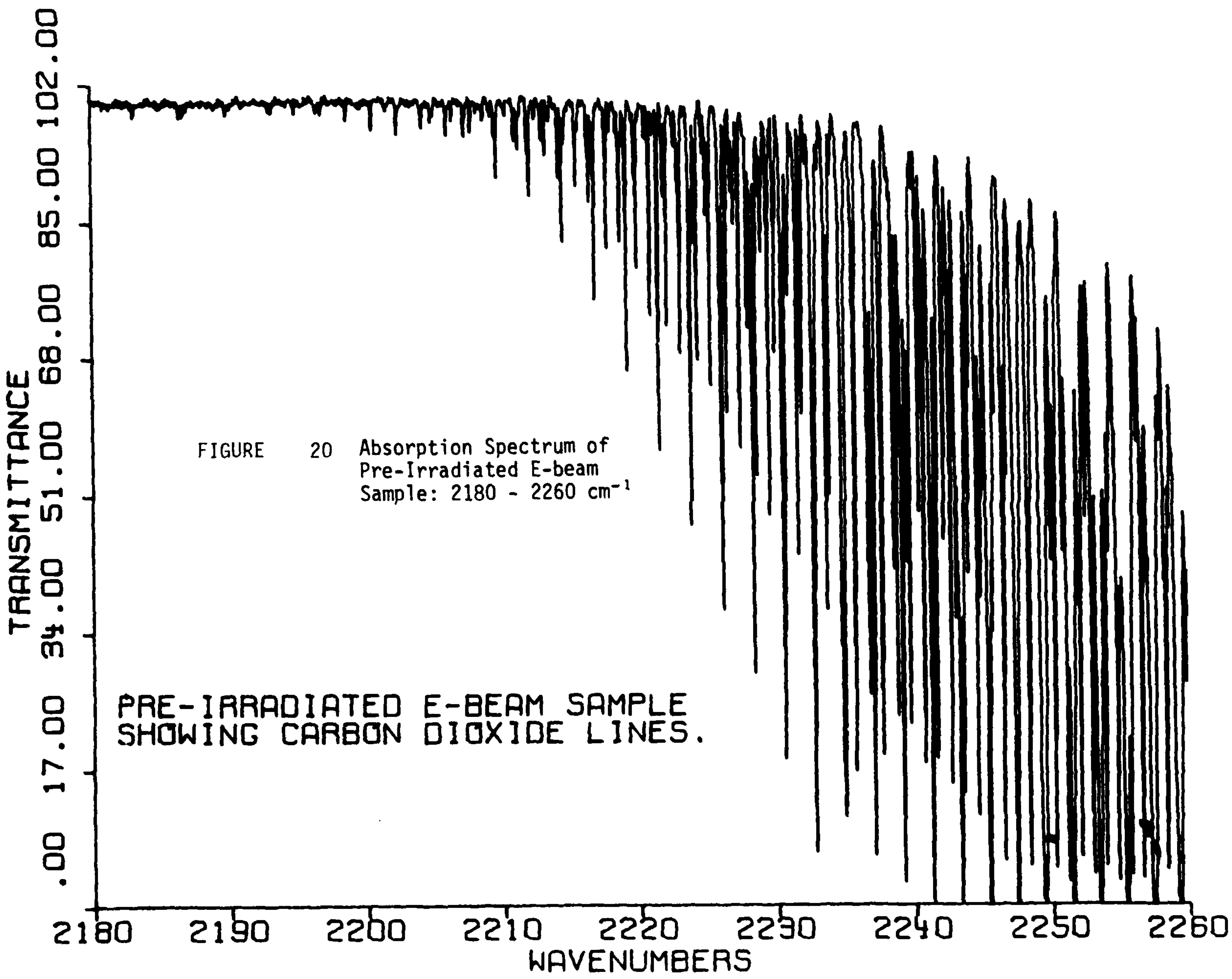


FIGURE 20 Absorption Spectrum of Pre-Irradiated E-beam Sample: 2180 - 2260 cm^{-1}

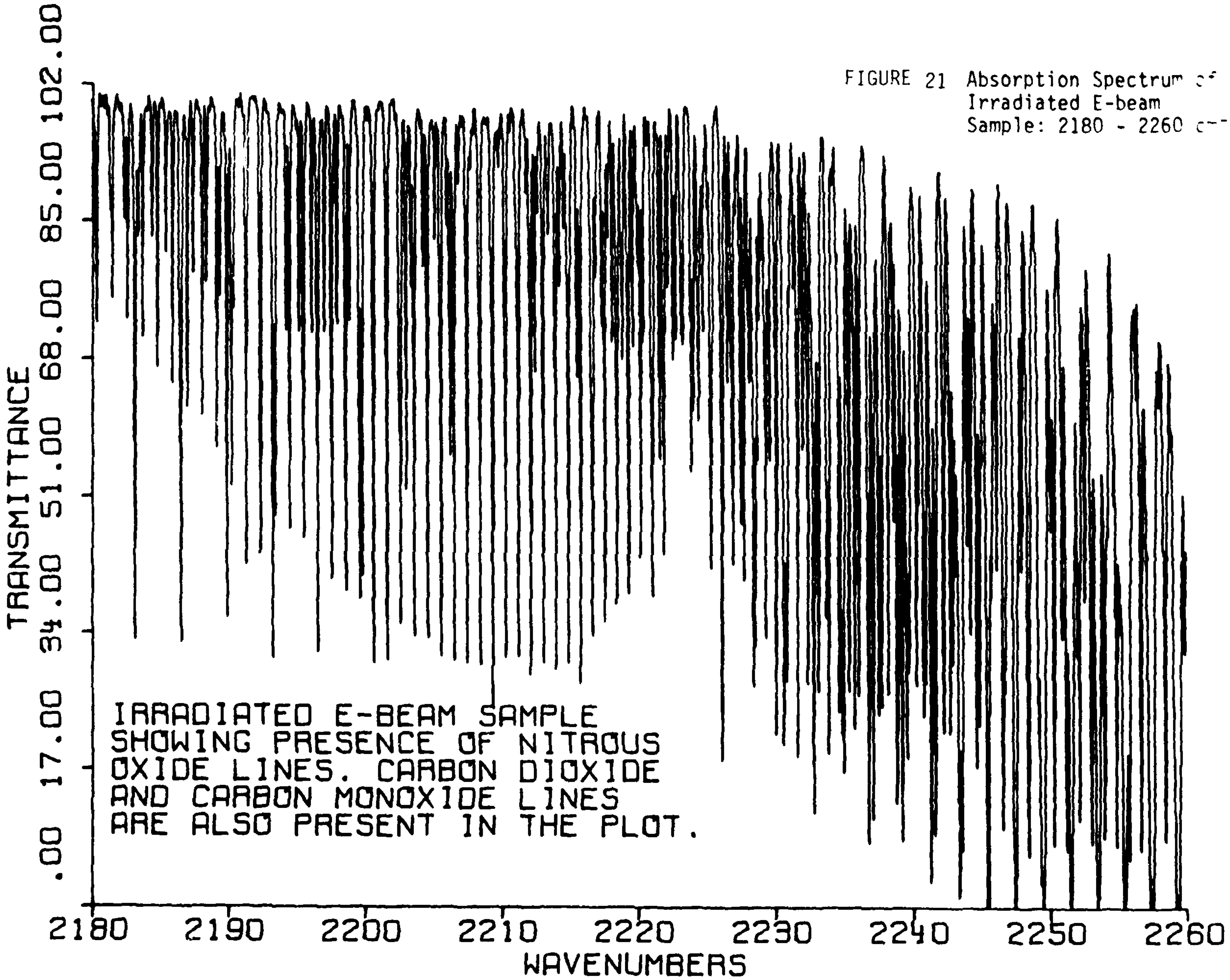
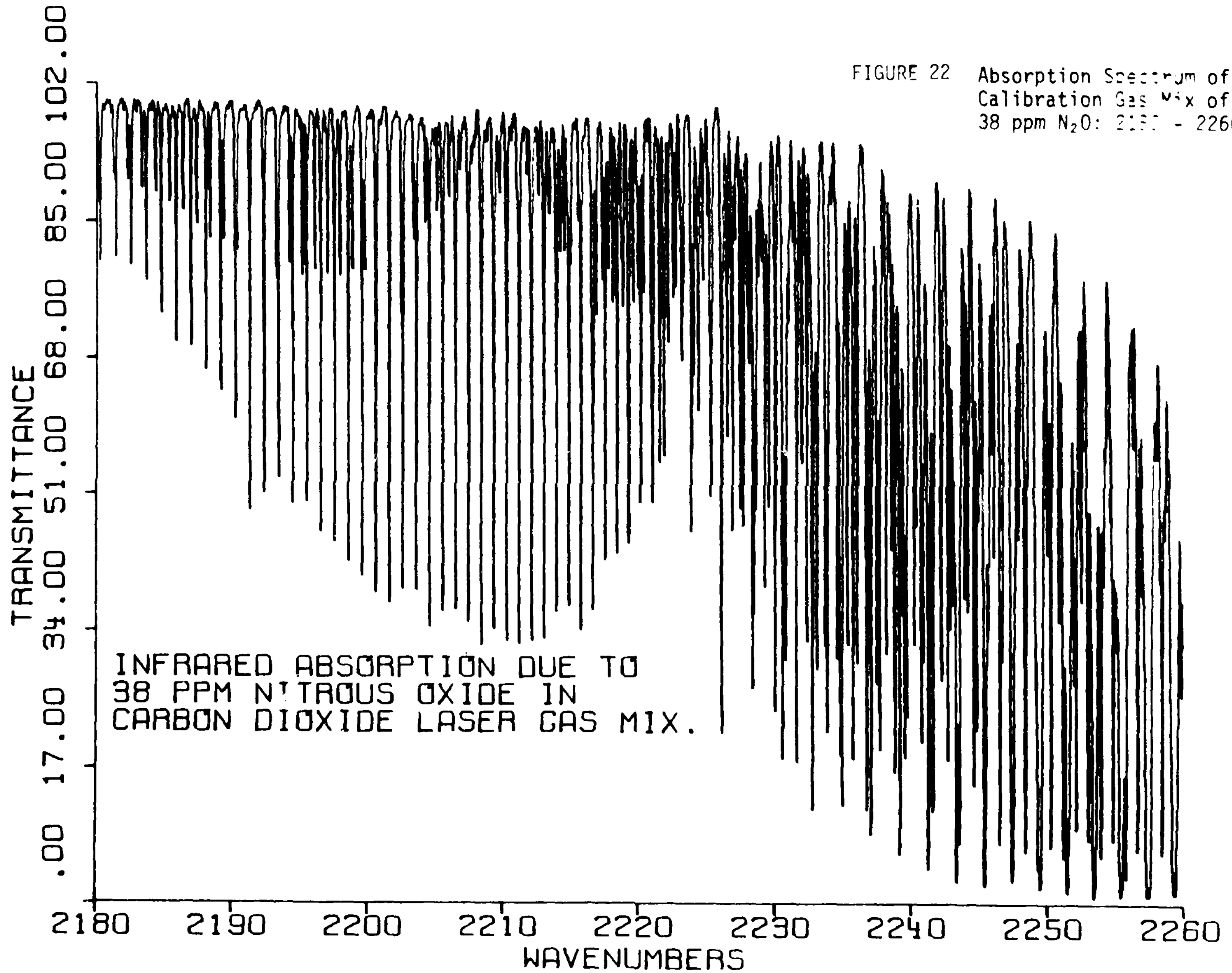


FIGURE 21 Absorption Spectrum of Irradiated E-beam Sample: 2180 - 2260 cm⁻¹

FIGURE 22 Absorption Spectrum of Calibration Gas Mix of 38 ppm N_2O: 2180 - 2260 cm^{-1}



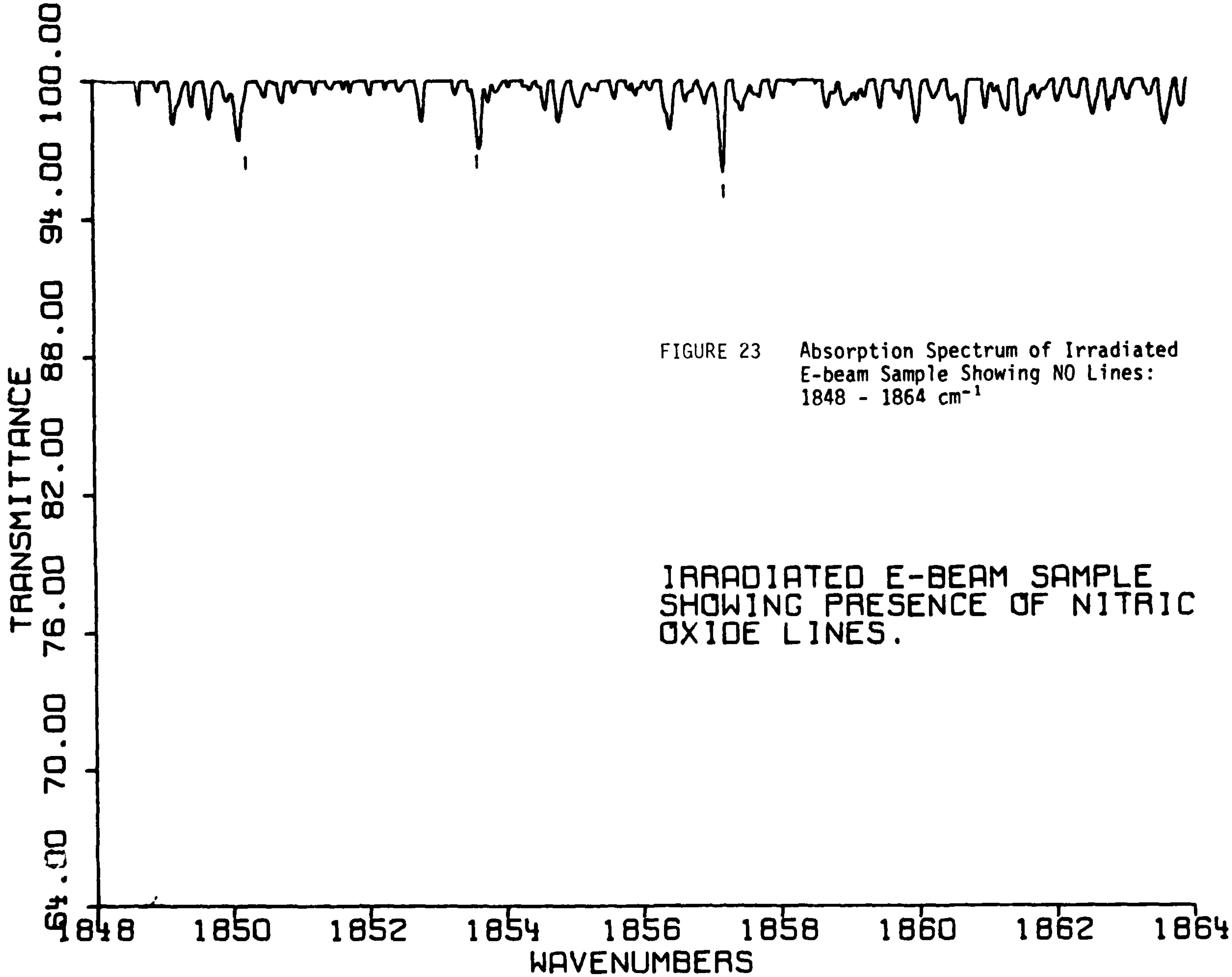


FIGURE 23 Absorption Spectrum of Irradiated E-beam Sample Showing NO Lines: 1848 - 1864 cm^{-1}

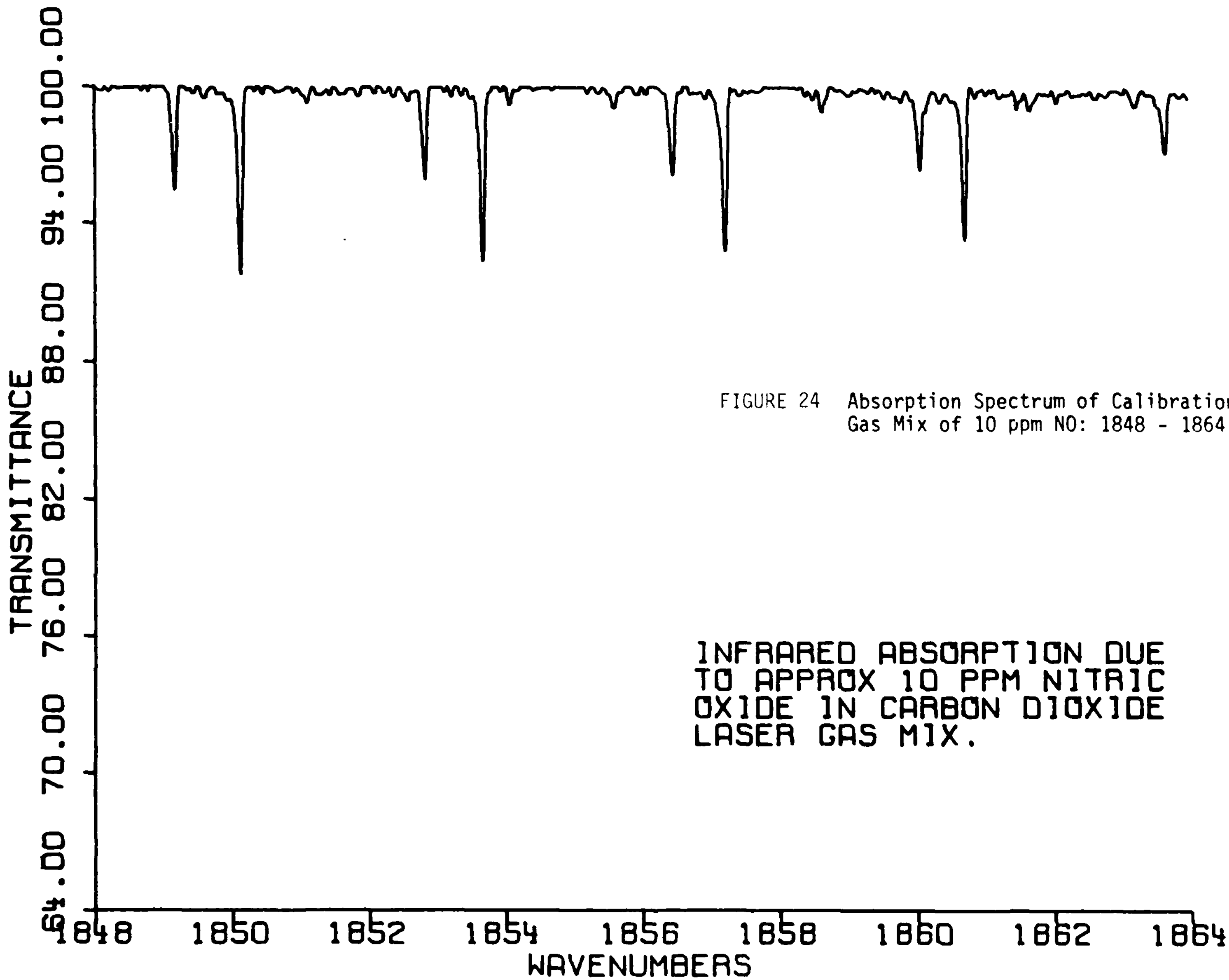


FIGURE 24 Absorption Spectrum of Calibration Gas Mix of 10 ppm NO: 1848 - 1864 cm^{-1}

Table 8 summarizes the results of the two data sets and includes estimates of the concentrations of the species present. No unusual spectral features were seen in either of the samples.

Measurements of the selected trace constituents in TEA laser gases have been obtained. The laser used is a Molectron model T250 run at about one-half atmosphere (actually a CO_2 TE laser). In the experiment, the laser is run sealed off for a specific number of pulses, then a gas sample is taken and analyzed. The limit on the number of pulses that can be run is determined by the onset of repeated arcing of the laser. Figure 25 shows the results obtained for one series of data runs of the laser. The gas mix used was made up of 260 torr of a 1:2:3 mix (CO_2:N_2:He) and 40 torr of H_2. Repetition rate for the laser was kept low to reduce gas heating and was about 0.75 Hz. Pulse width was roughly 1 μsec and voltage was about 25Kv. In all of the TE laser results, the predominant NO_x compound is NO, while in most of the EBCC data (at atmospheric pressure) the predominant species is N_2O. The only exception to this was some EBCC data taken after only one-half hour irradiation of the gas. In this very short irradiation, no N_2O lines were seen while the weaker NO lines are measureable. Thus, it appears that except for very short runs of the E-beam, the predominant nitrogen oxide is N_2O while in all the TE laser samples taken so far, NO is predominant. In all cases, no NO_2 could be detected.

A systematic study was performed of gas decomposition in the EBCC discharge and the effect of hydrogen and oxygen as gas additives. The results were presented at the 1979 Gaseous Electronics Conference [24]. For all the results presented here, the laser was operated with 250 Torr of CO_2 and 500 Torr of N_2 for a period of one hour before the gas was analyzed.

TABLE 8

ESTIMATES OF MINOR SPECIES CONCENTRATIONS IN EBCC GAS SAMPLES

Species	Estimated Concentration (ppm) 2 Hours RUN	7 Hour RUN
CO	120 ± 10	200 ± 10
N_2O	< .8	47 ± 3
NO	< 1	5 ± 2
NO_2	< 2	< 2

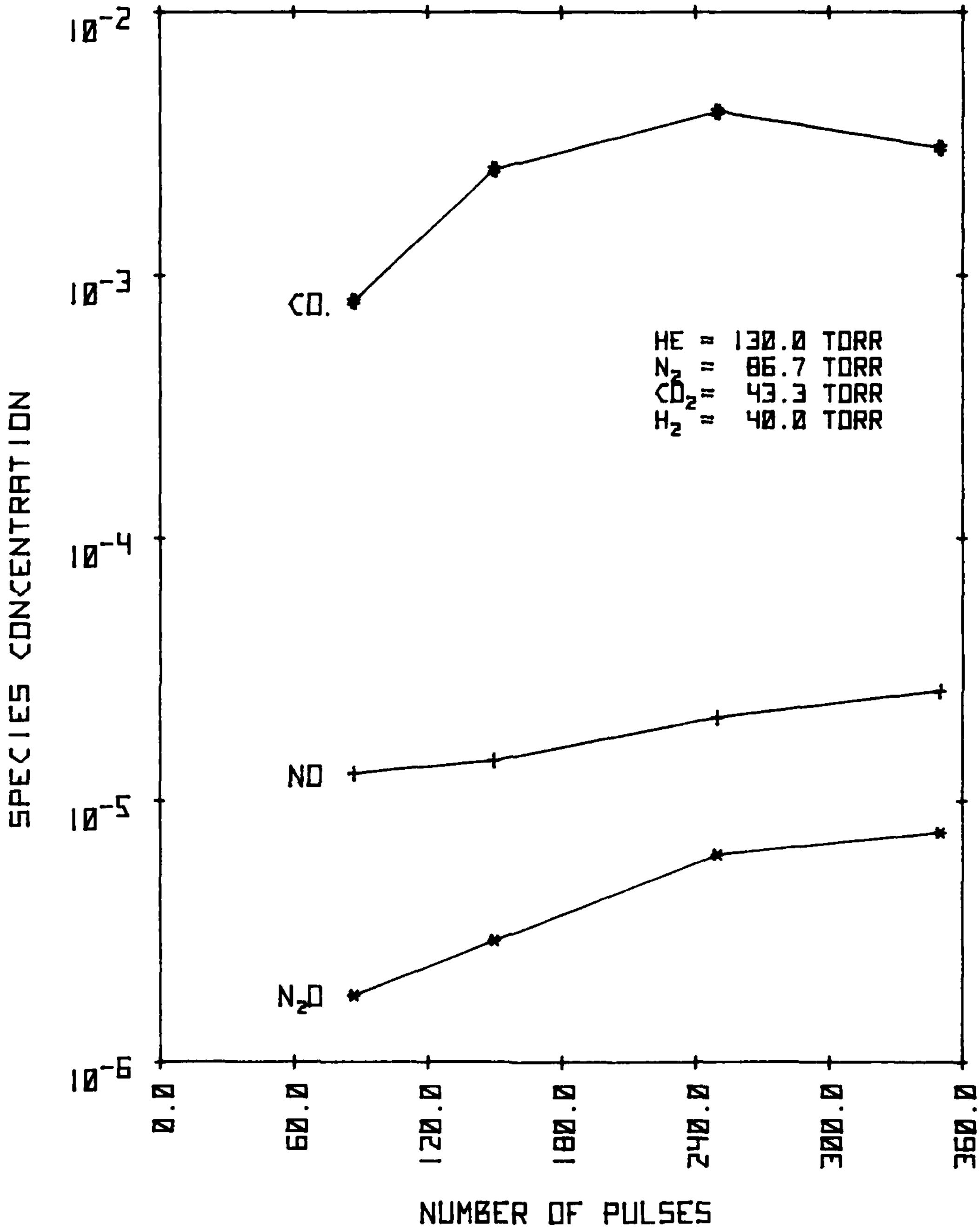


FIGURE 25 MINOR SPECIES BUILD UP IN A CO_2 TE LASER

With a pure N_2/CO_2 gas mix the oxides of nitrogen built up to the 10 ppm (parts per million) range while the CO concentration was of the order of a few hundred ppm. On line absorption measurements with the tunable diode laser showed that the build up of CO was very rapid when the laser was initially turned on, and reached a stable value after a few hundred seconds.

This laser system has very good vacuum capabilities, whereas most other laser systems have larger vacuum leaks. A small amount of oxygen was added to the gas mix to simulate the more usual conditions. The results, shown in Figure 26, indicate an increase in both CO and the oxides of nitrogen. At a pressure of five Torr added oxygen, the concentration of CO, N_2O, NO_2 and NO are increased by factors of 8,20, 12, and 6 respectively over the results obtained without added oxygen. Prior to the experiment, it was expected that the additional oxygen would react with CO to reform CO_2 lowering the CO concentration. Instead the oxygen appears to enhance the formation of CO.

The effect of adding hydrogen was investigated since many CO_2 systems now use gas mixtures containing hydrogen [25]. As shown in Figure 27, NO and NO_2 concentrations decrease with added hydrogen. The behavior of N_2O might be explained by dissociation of HNO_2 or HNO_3 formed in the discharge from NO and NO_2. No HNO_3 or HNO_2 was observed in the gas mix, but wouldn't be expected in large quantities if their destruction to N_2O was rapid compared to their formation. The sensitivity to HNO_3 detection was estimated at 10 ppm.

As hydrogen is added to the gas mix the concentrations of both CO and H_2O increase. This may be because the hydrogen reacts with the dissociatively produced oxygen to prevent the back reaction of CO to reform CO_2.

Finally hydrogen and oxygen were added together to the laser gas mix, with the results as shown in Figure 28. As before the concentration of NO and NO_2 after one hour irradiation was smaller when hydrogen was added than

FIGURE 26 Effect of added oxygen on minor species concentration of an E B C C SYSTEM

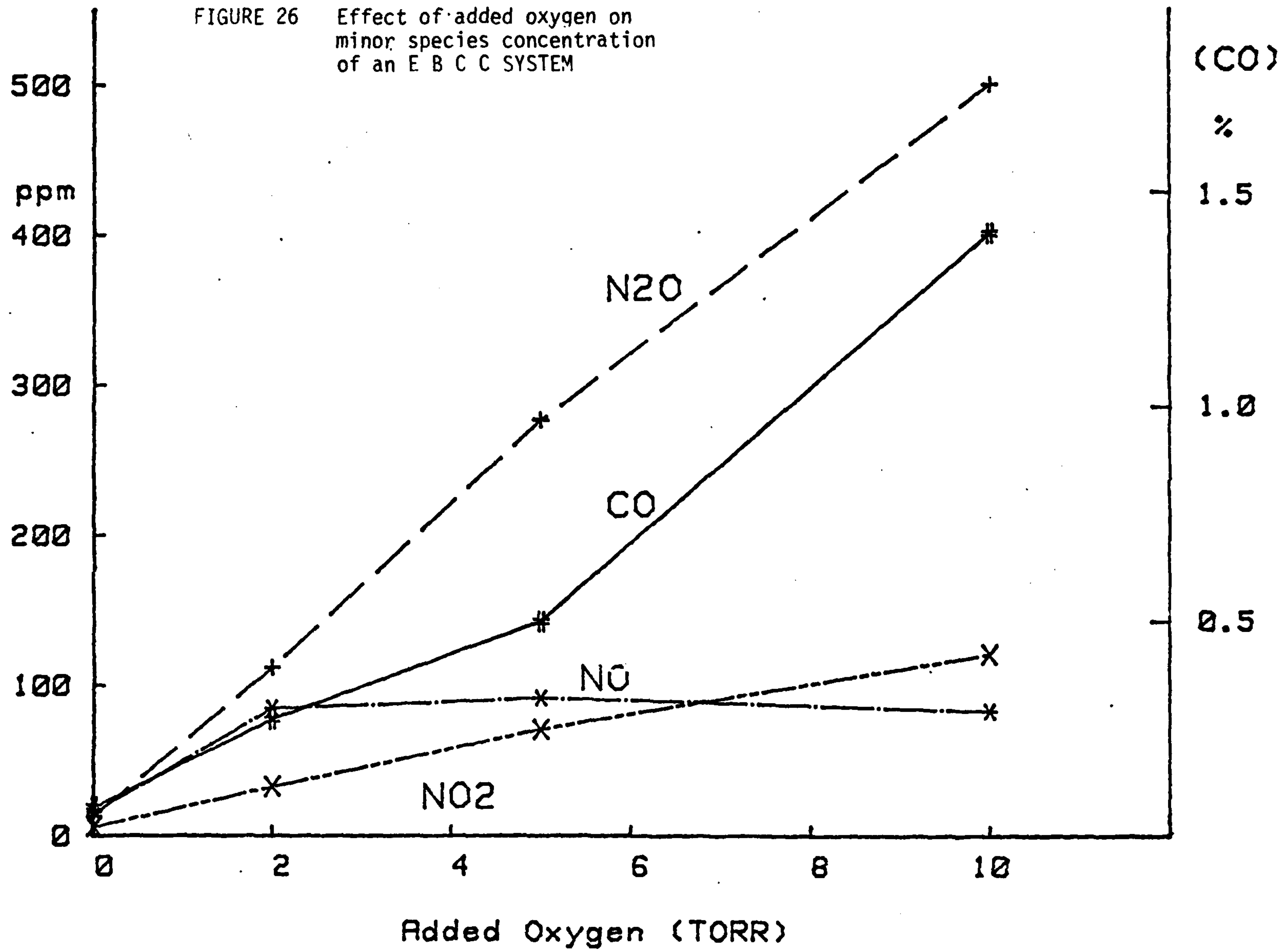


FIGURE 27

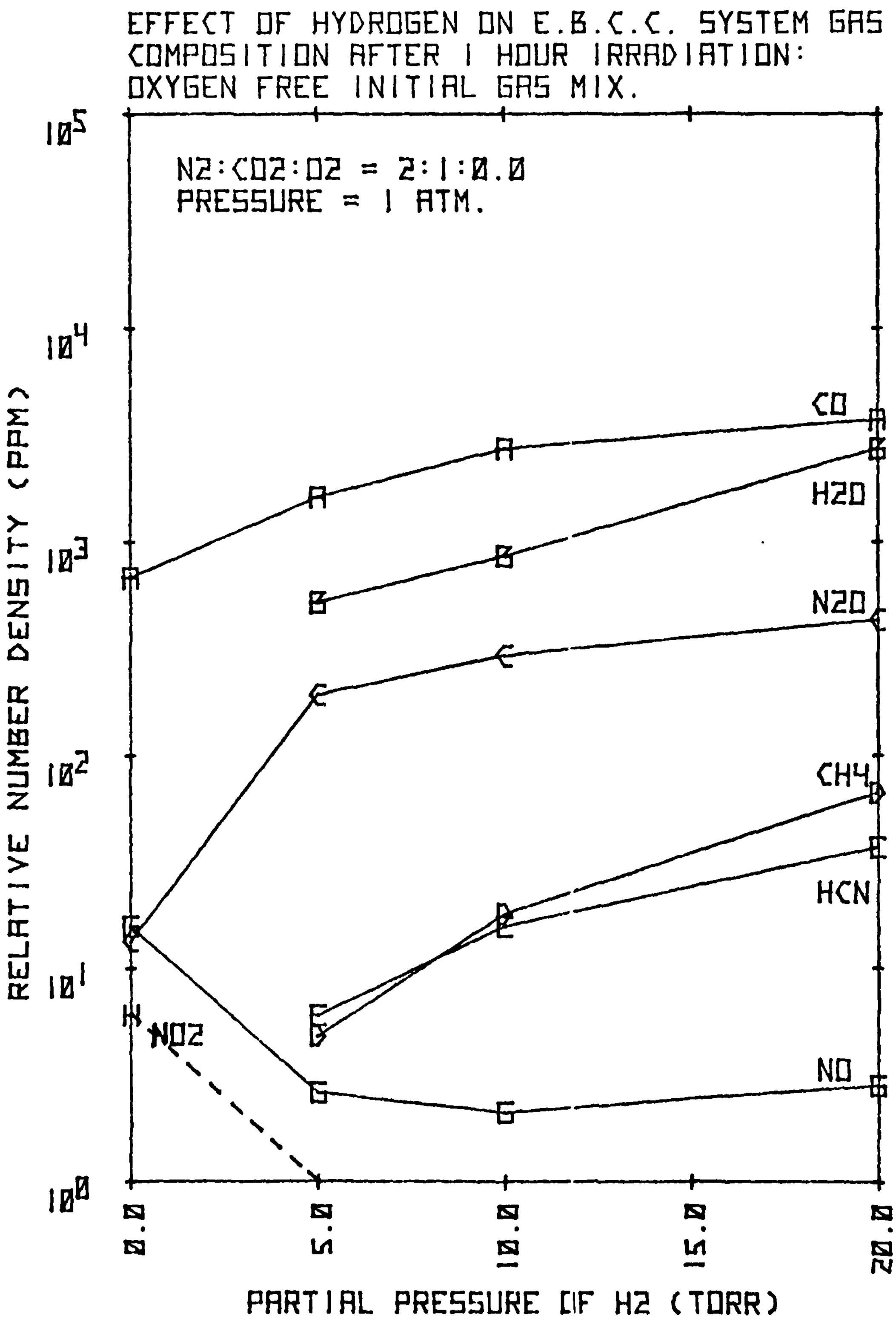
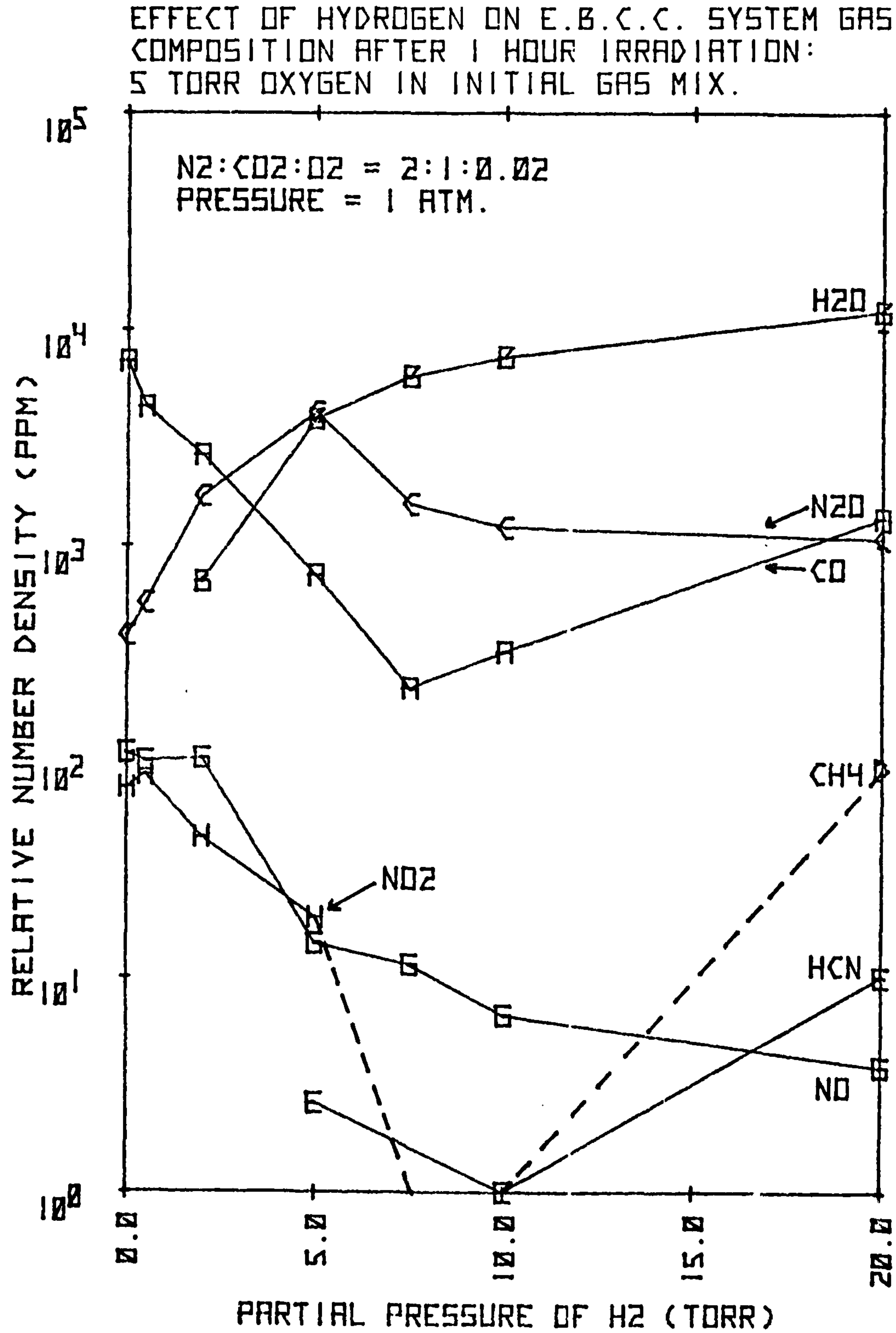

EFFECT OF HYDROGEN ON E.B.C.C. SYSTEM GAS
COMPOSITION AFTER 1 HOUR IRRADIATION:
OXYGEN FREE INITIAL GAS MIX.
N2:CO2:O2 = 2:1:0.0
PRESSURE = 1 ATM.
10^5
10^4
10^3
10^2
10^1
10^0
RELATIVE NUMBER DENSITY (PPM)
CO
H2O
N2O
CH4
HCN
NO
NO2
0.0
5.0
10.0
15.0
20.0
PARTIAL PRESSURE OF H2 (TORR)

FIGURE 28



EFFECT OF HYDROGEN ON E.B.C.C. SYSTEM GAS COMPOSITION AFTER 1 HOUR IRRADIATION: 5 TORR OXYGEN IN INITIAL GAS MIX.
N2:CO2:O2 = 2:1:0.02
PRESSURE = 1 ATM.
H2O
N2O
CO
CH4
NO2
HCN
NO
RELATIVE NUMBER DENSITY (PPM)
PARTIAL PRESSURE OF H2 (TORR)

when hydrogen was absent. However the concentration of NO, NO_2 and N_2O is greater for a given amount of hydrogen when both hydrogen and oxygen were added than when hydrogen alone was added. The CO concentration drops to a level below that observed in the basic N_2:CO_2 mix. To explain the behavior of CO two competing effects must be considered. The presence of H_2 lowers the concentration of discharge produced oxygen and tends to increase the CO level by preventing its back reaction of reform CO_2. It also appears that H_2O tends to reduce the CO concentration. The catalytic reaction of H_2O with CO to form CO_2 has previously been observed. As in the previous case, CH_4 and HCN appear, but only at higher H_2 concentrations.

In conclusion, the addition of oxygen to the gas mix greatly increases the production of nitrogen oxides and carbon monoxide. The addition of hydrogen to an oxygen free gas mix produces water at $\sim$10% of the H_2 concentration, increases the production of N_2O and CO while decreasing NO and NO_2.

The addition of hydrogen and a fixed quantity of oxygen to the gas mix produces water at 55% of the original H_2 concentration (up to twice the added O_2 concentration), increases the N_2O production but decreases that of CO, NO, and NO_2. When hydrogen was added to the mix, with or without oxygen, CH_4 and HCN were produced, but no HNO_3 or HNO_2 was detected in the irradiated gas mix.

REFERENCES

1. Cole, A.R.H., Tables of Wave Numbers for the Calibration of Infrared Spectrometers, 2nd ed., Pergamon Press (1977).

2. Bell, John Robert, Introductory Fourier Transform Spectroscopy, Academic Press (1972).

3. Lawson, J.L. and Uhlenbeck, G.E., Threshold Signals, M.I.T. Radiation Laboratory Series Vol. 34, McGraw-Hill Book Company, Inc. (1950).

4. Marquardt, D.W., J. Soc. Ind. Appl. Math., 11, 431 (1963).

5. Bevington, P.R., Data Reduction and Error Analysis for the Physical Sciences, McGraw-Hill Book Company, 1969.

6. Treanor, C.E., Rich, J.W., and R.G. Rehm, J. Chem. Phys., 48, 1798 (1968).

7. McClatchey, et. al., "AFCRL Atmospheric Absorption Line Parameters Complication,", AFCRL-TR-73-0096 (26 Jan. 1973).

8. Amiot, C. and Guelachvili, G., "Extension of 10^6 Samples Fourier Spectrometry to the Indium Antimonide Region: Vibration-Rotation Bands of $^{14}N_2\ ^{16}O$: 3.5-5.5 μm Region", J. Mol. Spec., 59, 171-190 (1976).

9. Young, L.G., "Compilation of Stratospheric Trace Gas Spectral Parameters", AFCRL-TR-76-0033 (15 Feb. 1976).

10. NO line positions were taken from a list supplied with the AFAPL/POD Tunable Diode Laser System. The measurements are from the Laboratoire De Spectronomie Moleculaire, Universite De Paris VI, however, it is not known if these line positions have been published.

11. Armstrong, B.H., "Spectrum Line Profiles: The Voight Function", J.Q.S.R.T., 18, 61 (1967).

12. Young, Lee A. and Eachus, James W., "Diopole Moment Function and Vibration Rotation Matrix Elements of CO", J. Chem. Phys., 44, 4195 (1966).

13. Draegert, D.A. and Williams, D., "Collisional Broadening of CO Absorption Lines by Foreign Gases", J. Opt. Soc. Am., 58, 1399 (1968).

14. Bouanich, J.P. and Brodbeck, C., "Measures Des Largeurs et Des Deplacements Des Raies De La Bande 0 → 2 De CO Autoperturbe at Perturbe Par N_2, O_2, H_2, HCL, NO, et CO_2", J.Q.S.R.T., 13 (1973).

15. Chackerian, Jr., C., "Electric Dipole Moment Function of the $X^1\Sigma^+$ State of CO: Vibration-Rotation Matrix Elements for Transitions of Gas Laser and Astrophysical Interest", J. Chem. Phys. 65, 4228 (1976).

16. Abels, L.L. and Shaw, J.H., "Widths and Strenghts of Vibration-Rotation Lines in the Fundamental Band of Nitric Oxide", J. Mol. Spec., 20, 11 (1966).

17. French, I.P. and Arnold, Jr., T.E., "Linewidth of the $J=1/2 \rightarrow 3/2$ Rotational Absorption in Nitric Oxide", J. Chem. Phys., 48, 5720 (1968).

18. Boissy, J.P., Valentin, A., Cardinet, Ph., Claude, M.L., and Henry A., "Line Intensities of the ν_3 Fundamental Band of Nitrous Oxide", J. Mol. Spec., 57, 391 (1975).

19. Toth, R.A., "Self-Broadened and N_2 Broadened Linewidths of N_2O", J. Mol. Spec., 40, 605 (1971).

20. Tejwani, G.D.T. and Veranasi, P., "Theoretical Line Widths in N_2O-N_2O and N_2O-Air Collisions", J.Q.S.R.T., 11, 1659 (1971).

21. French, I.P. and Arnold, Jr., T.E., "Foreign-Gas Broadening of the $J=5 \rightarrow 6$ Rotational Transition of Nitrous Oxide", J. Mol. Spec., 27, 218 (1968).

22. Lowder, J.E., "Band Intensity and Line Half-Width Measurements in N_2O Near 4.5 μ", J.Q.S.R.T., 12, 873 (1972).

23. Young, L.D.G., "Relative Intensity Calculations for Nitrous Oxide", J.Q.S.R.T., 12, 307 (1972).

24. P. Bletzinger and C.A. DeJoseph Jr., "Effect of Oxygen and Hydrogen on Electron Beam Discharges in Atmospheric Pressure CO_2 Mixtures", paper H-2 at Gaseous Electronics Conference, Pittsburgh (1979).

25. Deutsch, T.F., "Effect of Hydrogen on CO_2 TEA Lasers", Appl. Phys. Lett., 20, 315 (1972).

Appendices

APPENDIX I

Description of the Fourier Transfrom Spectrometer Calibration program FTCAL. This program is a modified version of a program appearing in Tables of Wave numbers for the Calibration of Infrared Spectrometers compiled by A.R.H. Cole, 2nd edition, Pergamon Press, 1977, pp. 202-205.

The program fits a set of up to 100 standard lines to one of two fitting functions. In normal usage, the standard lines are fit to the function,

$$\sigma(\text{standard}) = \sigma_1 \cdot \frac{n(\text{HeNe})}{n(\sigma_1)} \tag{A-1}$$

where,

$$\sigma_1 = \frac{\sigma(\text{measured})}{1-a} \tag{A-2}$$

and the parameter 'a' is determined by the method of least-squares. n(HeNe) and $n(\sigma_1)$ are the indices of refraction of air at the wavenumber of the helium-neon laser and wavenumber σ_1. The program may also be used to fit the standard lines to a non-linear function of the form,

$$\sigma_1 = a_1 + a_2\sigma + a_3\sigma^2 + a_4\sigma^3 \tag{A-3}$$

where σ is the measured line position and the a_i's are determined by least-squares. The fitting function used is determined by the user by setting the parameter SWITCH to either 1 or 0. After the fitting functions is determined, measured line positions of unknown lines are read-in and corrected according to either equation (A-2) or (A-3) and equation (A-1). For extrapolation out of the wavenumber region of the standard lines, equation (A-3) (SWITCH = 0) should not be used. For interpolation within the wavenumber region on the standard lines, either equation (A-2) or (A-3) may be used.

Description of the input parameters:

PR - Sets the maximum allowable error (in cm^{-1}) between the corrected measurements and the known values of the standard lines used. After a least-squares fit is made to the known standards, the maximum error is found between the corrected measurements and the known line positions of the standards. If this maximum error exceeds the value PR, the measurement that yielded this error is removed from the set of measured values and the least-squares fit is repeated. This rejection process continues until the maximum error no longer exceeds PR. If PR = 0, all measured values are used.

SWITCH - This parameter determines which fitting function is chosen. If SWITCH = 1, equation (A-2), which is linear in the measured values, is used. If SWITCH = 0, equation (A-3), which is non-linear in the measured values, is used.

TEMPC and PRESC - The air temperature (deg. C) and barometric pressure (mm of Hg) at which the standard lines were measured.

TEMPU and PRESU - The air temperature (deg. C) and barometric pressure (mm of Hg) at which the standard lines were measured.

Some additional notes to the user of FTCAL are in order. All cards read by FTCAL except the first card, are read in the list directed read format of the CDC6600. Data may be placed anywhere on a card and if more than one parameter is to be read from a card, the parameters may be separated by spaces, commas, or other symbols (see CDC6600 manual). The first number on a standard line card and an unknown line card are for line indentification. For standard lines this can be an integer from 0 to 999; for unknown lines this can be an integer from 0 to 9999. If the number of standard lines used is less than that needed for a least-squares fit to the fitting function chosen (SWITCH = 0), the function is truncated starting with the highest powers of the measured values.

A listing of FTCAL is given on the following pages. The comment cards explain the order that the data should appear on cards.

```
      PROGRAM FTCAL(INPUT,OUTPUT)
C     CALIBRATION PROGRAM FOR FOURIER TRANSFORM SPECTROMETER
C         FIRST CARD-COLS 1-50 FOR A TITLE
C         SECOND CARD-PR (REJECTION CRITERIA)
C         THIRD CARD-SWITCH (1=LINEAR FIT, 0=CUBIC FIT)
C         FOURTH CARD IS FOR TEMP.(DEG C) AND BAROMETRIC PRESSURE(MM HG)
C           AT WHICH THE STANDARD LINES WERE MEASURED
C         STANDARD LINES FOLLOW-MAXIMUM NUMBER IS 100
C               FIRST NUMBER ON THE CARD IS FOR LINE IDENTIFICATION
C               SECOND NUMBER IS FOR THE LINE POSITION MEASUREMENT
C               THIRD NUMBER IS FOR WAVENUMBER OF STANDARD LINE
C         THE LAST CARD WITH A KNOWN WAVENUMBER TO BE USED FOR
C           CALIBRATION MUST BE FOLLOWED BY A CARD WITH THREE ZEROS
C           PUNCHED WITH SPACES BETWEEN ZEROS
C         NEXT CARD IS FOR TEMP. AND PRES DATA FOR UNKNOWNS
C         UNKNOWN LINES FOLLOW-SAME FORMAT AS STANDARD LINES BUT WITHOUT
C           WAVENUMBER
C         MORE THAN ONE BATCH OF STANDARDS AND UNKNOWNS CAN BE RUN IN
C           SUCCESSION IF A CARD WITH -1 IS PLACED BETWEEN BATCHES
C         THE LAST CARD IN THE DECK MUST BE THREE ZEROS AS ABOVE
C
C     READ AND WRITE STATEMENTS ARE FOR CDC6600 ONLY
C
      DOUBLE PRECISION DEX,VNU,TE,PE,HENEX,C,A,D,P,Q,CE,CN,C1
      DIMENSION D(10),A(4,5),C(100,10),TITLE(12)
C
C     FUNCTION DEX IS THE INDEX OF REFRACTION OF THE AIR MINUS ONE
C
      DEX(V,TE,PE)=(6.4328D-05+2.94981D06/(1.46D10-V*V)+2.5540D04/(4.1D09
     6-V*V))*1.0549D0/(1.0D0+3.66D-03*TE)*PE/7.6D02
   10 READ1010,(TITLE(I),I=1,12)
 1010 FORMAT(12A5)
      READ*,PR
      READ*,SWITCH
      READ*,TEMPC,PRESC
      TE=TEMPC
      PE=PRESC
      HENEX=DEX(1.5798D04,TE,PE)+1.0D0
      ISWTCH=SWITCH
      N=0
C
C     READ STANDARD LINES ONE AT A TIME AND SET UP ARRAY FOR LEAST
C     SQUARES TREATMENT
C
   20 READ*,DN1,A1,W1
      IF(A1.EQ.0.)GO TO 35
      N=N+1
      C1=A1
      C(N,1)=1.0D0
      C(N,2)=C1
      C(N,3)=C1*C1
      C(N,4)=C1*C1*C1
C
C     THE NEXT TWO STATEMENTS CORRECT FOR THE DISPERSION OF THE INDEX
C     OF REFRACTION OF THE AIR BETWEEN THE STANDARDS AND THE HENE-LASER
C
      VNU=W1
```

```
      C(N,9)=VNU*(DLX(VNU,TE,PL)+1.000)/HENEX
      C(N,5)=DN1
      C(N,7)=A1
      C(N,10)=W1
      GO TO 20
   35 NNN=N
C
C     LEAST SQUARES FIT
C
   40 DO 50 I=1,4
      DO 50 J=1,5
   50 A(I,J)=0.000
      IF(ISWTCH.EQ.0)GO TO 55
      MM1=2
      MM=1
      DO 53 J=1,N
   53 A(2,2)=A(2,2)+(C(J,5)-C(J,2))/C(J,3)
      CN=N
      A(2,2)=1.000/(1.000-A(2,2)/CN)
      GO TO 150
   55 IF(N-4)60,60,80
   60 DO 70 J=1,N
      A(J,N+1)=C(J,5)
      DO 70 K=1,N
   70 A(J,K)=C(J,K)
      MM=N
      MM1=N+1
      GO TO 100
   80 DO 90 L=1,4
      DO 90 K=1,5
      DO 90 J=1,N
   90 A(L,K)=A(L,K)+C(J,L)*C(J,K)
      MM=4
      MM1=5
  100 DO 150 J=1,MM
      P=1.000/A(J,J)
      DO 110 K=J,MM1
  110 A(J,K)=P*A(J,K)
      DO 140 L=1,MM
      IF(L-J)120,140,120
  120 Q=A(L,J)
      DO 130 K=J,MM1
      A(L,K)=A(L,K)-Q*A(J,K)
  130 CONTINUE
  140 CONTINUE
  150 CONTINUE
C
C     SET UP THE ARRAYS OF CALCULATED STANDARD POSITIONS AND DIFFERENCES
C
  155 DO 160 J=1,NNN
      C2=C(J,2)
      VNU=A(1,MM1)+C2*(A(2,MM1)+C2*(A(3,MM1)+C2*A(4,MM1)))
C
C     THE NEXT STATEMENT IS THE DISPERSION CORRECTION
C
      C(J,9)=VNU*HENEX/(DLX(VNU,TE,PL)+1.000)
      C(J,8)=C(J,10)-C(J,9)
```

```
        160 CONTINUE
C
C           REJECTION ROUTINE
C
        170 IF(PR)280,280,180
        180 X=0.
            DO 230 J=1,N
            IF(C(J,8))190,200,200
        190 Y=-C(J,8)
            GO TO 210
        200 Y=C(J,8)
        210 IF(Y-X)230,230,220
        220 NN=J
            X=Y
        230 CONTINUE
            IF(PR-X)240,280,280
        240 DO 250 J=1,10
            D(J)=C(NN,J)
        250 C(NN,J)=0.
            NN=NN+1
            DO 260 M=1,10
            DO 260 J=NN,N
        260 C(J-1,M)=C(J,M)
            DO 270 J=1,10
        270 C(N,J)=D(J)
C
C           GO BACK AND DO LEAST SQUARES
C
            N=N-1
            GO TO 40
        280 PRINT1040,(TITLE(I),I=1,12)
       1040 FORMAT(1H1,12A5)
            PRINT1050,N,PR
       1050 FORMAT(1H0,17HNO. OF STD LINES=,I3,17H REJECTION LIMIT=,F5.3)
            PRINT1052,TEMPC
            PRINT1053,PR.SC
       1052 FORMAT(1H0,35HTEMPERATURE DURING CALIBRATION RUN=,F5.1,6H DEG.C)
       1053 FORMAT(1H ,20HBAROMETRIC PRESSURE=,F6.1,7H MM HG.)
            IF(ISWTCH.EQ.0)GO TO 285
            PRINT1055
       1055 FORMAT(1H0,40HLINEAR CORRECTION IN EFFECT-CONSTANT IS:)
            PRINT1070,A(2,MM1)
            GO TO 288
        285 PRINT1060
       1060 FORMAT(1H0,22HCONSTANTS OF CUBIC EQN)
            PRINT1070,(A(J,MM1),J=1,MM)
       1070 FORMAT(1H ,5X,E17.10)
        288 PRINT1080
       1080 FORMAT(1H0,80H NO.                MEAS                  NU(STD)
          6     NU(CALC)              DIFF)
            DO 300 J=1,NNN
            IN1=C(J,6)
            A2=C(J,7)
            W1=C(J,10)
            W2=C(J,9)
            DIF=C(J,8)
            IF(J.GT.N)GO TO 290
```

```
      PRINT1100,IN1,A2,W1,W2,DIF
 1100 FORMAT(1H ,I3,9X,F9.3,12X,F10.4,12X,F9.3,9X,F7.3)
      GO TO 300
  200 PRINT1200,IN1,A2,W1,W2,DIF
 1200 FORMAT(1H ,I3,9X,F9.3,12X,F10.4,12X,F9.3,9X,F7.3,1H*)
  300 CONTINUE
      IF(N-NNN)310,320,320
  310 PRINT1100
 1100 FORMAT(1H ,15H*=REJECTED LINE)
  320 PRINT1110
 1110 FORMAT(1H0,8H RESULTS)
      READ*,TEMPU,PRESU
      TE=TEMPU
      PE=PRESU
      PRINT1130,TEMPU
      PRINT1155,PRESU
 1130 FORMAT(1H0,31HTEMPERATURE DURING UNKNOWN RUN=,F5.1,6H DEG.C)
      HENEX=DEX(1.579800D4,TE,PE)+1.0D0
      PRINT1120
 1120 FORMAT(1H0,64H NO.               MEAS                          WAVE
     6NUMBER(CALC))
C
C     READ A LINE TO BE CALIBRATED
C
  330 READ*,DN1,A2
      IN1=DN1
      IF(IN1.LT.0)GO TO 10
      IF(A2.EQ.0.0)STOP
      C2=A2
C
C     THE NEXT TWO STATEMENTS ARE THE LEAST-SQUARES ADJUSTMENT AND THE
C     DISPERSION CORRECTION
C
      VNU=A(1,MM1)+C2*(A(2,MM1)+C2*(A(3,MM1)+C2*A(4,MM1)))
      W2=VNU*HENEX/(DEX(VNU,TE,PE)+1.0D0)
      PRINT1140,IN1,A2,W2
 1140 FORMAT(1H ,I4,9X,F9.3,34X,F9.3)
      GO TO 330
      END
```

APPENDIX II

On the following pages is a listing of the program CODIAG and its associated subroutines and function subprograms. The programs are well commented so little explanation will be given here. One important point is worth mentioning. The parameter NDP (fourth card, first number) determines the assumed resolution of the interferometer. It should reflect any effects due to finite source size and should only include data points on one side of the interferogram.

```
      PROGRAM CODIAG(INPUT,OUTPUT,PLOT)
C
C     THIS IS THE MAIN DRIVING PROGRAM FOR DETERMING THE ROTATIONAL
C     TEMPERATURE AND THE VIBRATIONAL POPULATION DISTRIBUTION OF CARBON
C     MONOXIDE BY OBSERVING THE INFRARED EMISSION FROM THE HOT GAS. THE
C     PROGRAM CAN BE USED WITH EMISSION SPECTRA FROM EITHER THE FUNDA-
C     MENTAL, FIRST OVERTONE, OR SECOND OVERTONE. INTENSITIES CAN BE
C     EITHER ABSOLUTE (WATTS/STERADIAN/WAVENUMBER) OR RELATIVE. THE
C     PROGRAM ASSUMES THAT THE INSTRUMENT RESOLUTION IS MUCH GREATER
C     THAN THE WIDTH OF THE LINES, AND ASSUMES INSTRUMENT FUNCTIONS
C     OF THE KIND EXPECTED FROM AN INTERFEROMETER.
C
C     SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
C       SUBROUTINE ROTEM(IPRNT,FNO,TEMP)
C         CALCULATES THE ROTATIONAL TEMPERATURE OF THE GAS
C       SUBROUTINE VIBDIS(IPRNT,XMEAS,YMEAS,NPV,VNCAL,IHIV,YOFFSET,TEMP)
C         CALCULATES THE VIBRATIONAL POPULATION DISTRIBUTION OF CO
C       SUBROUTINE SPECGN(ANV,LEVEL,YOFFSET,TEMP,WMIN,WMAX,WOUT,YOUT,NN)
C         CALCULATES A THEORETICAL EMISSION SPECTRUM USING THE
C         VIBRATIONAL DISTRIBUTION AND ROTATIONAL TEMPERATURE CALCULATED
C       SUBROUTINE PLOTTOR(XTHERY,YTHERY,NTHERY,XDATA,YDATA,NDATA,FXF,FL
C         AF,CXF,FYL,FLYE,CYE,IOPTN,LABEL)
C         MAKES A PLOT OF THE THEORETICAL SPECTRUM CALCULATED IN SPECGN
C         AND PLOTS THE MEASURED DATA ON THE SAME SET OF AXES
C
C     A NUMBER OF OTHER SUBROUTINES AND FUNCTION SUBPROGRAMS ARE CALLED
C     BY THE ABOVE ROUTINES. THE USER OF THIS PROGRAM IS REFERED TO THE
C     COMMENTS IN THE ABOVE ROUTINES FOR A LIST OF THESE ADDITIONAL
C     ROUTINES REQUIRED.
C
C     WITH THE EXCEPTION OF THE FIRST TWO DATA CARDS, ALL DATA IS READ
C     IN THE LIST DIRECTED READ FORMAT OF THE CDC6600. IN THIS FORMAT,
C     DATA MAY APPEAR ANYWHERE ON A CARD AND MAY BE SEPARATED BY BLANK
C     SPACES, COMMAS, ECT. THE USER IS REFERED TO THE CDC6600 FORTRAN
C     EXTENDED REFERENCE MANUAL FOR A COMPLETE DESCRIPTION OF THIS
C     FORMAT.
C
C     DATA CARDS
C       FIRST CARD - COLUMNS 1-80 FOR A TITLE
C       SECOND CARD- COLUMNS 1-20 FOR DATE AND RUN NUMBER
C       THIRD CARD - 1ST NUMBER IS DELTA V FOR THE DATA BEING USED.
C                    2ND NUMBER IS TO INDICATE IF INTENSITIES ARE
C                    ABSOLUTE- 0=RELATIVE INTENSITIES, 1=ABSOLUTE
C       FOURTH CARD- CONTAINS FOUR PARAMETERS ASSOCIATED WITH THE
C                    INTERFEROMETER AND PRETAINING TO THE DATA COLLEC-
C                    TION. THEY ARE AS FOLLOWS
C                    1ST NUMBER-NUMBER OF DATA POINTS TAKEN
C                    2ND NUMBER-NUMBER OF TRANSFORM POINTS
C                    3RD NUMBER-HOLLERITH CHARACTERS DESCRIBING THE
C                    APODIZATION FUNCTION USED IN THE TRANSFORM.
C                    ONE OF THREE CAN BE USED
C                    BX-BOXCAR APODIZATION
C                    TI-TRIANGULAR APODIZATION
C                    HG-HAPP GENZEL APODIZATION
C                    (IN THE LIST DIRECTED READ FORMAT, HOLLERITH
C                    CHARACTERS MUST BE IN QUOTES, SUCH AS "HG")
C                    4TH NUMBER-THE SAMPLE SPACING OF THE DATA POINTS
```

```
C                 IN UNITS OF HALF-WAVELENGTH OF THE HENE LASER
C     FIFTH CARD - PRINTOUT CONTROL FOR ROTEM, 0=NO PRINTOUT
C                 1=DATA FROM ROTEM IS PRINTED OUT
C     SIXTH THRU NTH CARD- DATA FOR USE IN ROTATIONAL TEMPERATURE
C                 DETERMINATION. 1ST NUMBER ON CARD SIX IS THE NUMBER
C                 OF DATA POINTS TO BE READ (UP TO 50). THE DATA
C                 POINTS FOLLOW: X(1),Y(1),X(2),Y(2),... AFTER THE
C                 LAST DATA POINT, THE ESTIMATED STANDARD DEVIATION
C                 OF THE INTENSITIES SHOULD BE PUNCHED.
C     NEXT CARD  - RPINT CONTROL FOR VIBDIS, EITHER 0,1,2, OR 3
C                 0-NO PRINTOUT FROM VIBDIS
C                 1-PRINTOUT OF POPULATION DISTRIBUTION AND LINE-
C                   PRINTER PLOT OF OCCUPATION NUMBERS
C                 2-STATISTICS FROM REGRES AND CALCULATED COEF.
C                 3-OPTIONS 1 PLUS 2
C     NEXT CARD THRU M CARDS- DATA FOR VIBDIS. JUST AS IN ROTEM, 1ST
C                 NUMBER IS THE NUMBER OF DATA POINTS (UP TO 100),
C                 THEN THE DATA POINTS, THEN THE STANDARD DEVIATION.
C     NEXT CARD  - 1ST NUMBER IS THE HIGHEST VIBRATIONAL LEVEL TO BE
C                 INCLUDED IN THE ANALYSIS (UP TO V=39). 2ND NUMBER
C                 IS THE CO PARTIAL PRESSURE (TORR).
C     NEXT CARD  - PLOT OPTION. 0=NO PLOT, 1=CALCOMP PLOT OF
C                 THEORETICAL SPECTRUM AND MEASURED DATA.
C     NEXT CARD(OPTIONAL)- IF A CALCOMP PLOT HAS BEEN REQUESTED, THIS
C                 CARD CONTAINS A NUMBER WHICH DESCRIBES VARIOUS PLOT
C                 OPTIONS. EITHER 0,1,2, OR 3
C                 0-NORMAL PLOT SEQUENCE. THEORETICAL SPECTRUM AND
C                   MEASURED DATA ARE PLOTTED AND THE USER MUST
C                   SPECIFY THE LIMITS ON THE X-AXIS AND Y-AXIS
C                 1-AS ABOVE EXCEPT NO MEASURED DATA IS PLOTTED
C                 2-AS IN 0 EXCEPT THE USER NEED ONLY SPECIFY THE
C                   LIMITS ON THE X-AXIS. THE YAXIS IS SCALED TO 8
C                   INCHES.
C                 3-AS IN 2 EXCEPT NO DATA IS PLOTTED
C     NEXT CARD(OPTIONAL)- IF A CALCOMP PLOT IS DESIRED, THIS CARD IS
C                 FOR SPECIFYING THE PLOT LIMITS ON THE X AND Y AXIS.
C                 1ST NUMBER-STARTING WAVENUMBER FOR THE X-AXIS
C                 2ND NUMBER-LAST WAVENUMBER FOR THE X-AXIS
C                 3RD NUMBER-CHANGE IN WAVENUMBER PER INCH
C                 4TH NUMBER-THE INTENSITY MINIMUM FOR THE Y-AXIS
C                 5TH NUMBER-THE INTENSITY MAXIMUM FOR THE Y-AXIS
C                 6TH NUMBER-CHANGE IN INTENSITY PER INCH
C                 (THE LAST THREE NUMBERS CAN BE ZEROS IF PLOT OPTION
C                 2 OR 3 ARE CHOSEN)
C     VERSION 02-26-78-1       FEB. 23, 1978        C. DEJOSEPH, JR.
      COMMON/Z/NUP,SSP,IAFN,NTP,IDELTAV,IFAB
      COMMON/W/WE,WEXE,WEYE,WEZE,WEAE,WEBE,BE,AE,GE,DE,DDE,BDE,PE,HE,ENE
      COMMON/SCALIT/NX,NY,NTX,NTY,LINPIN,IGRID
      COMMON/FF/XTHERY(2000),YTHERY(2000)
      DIMENSION TITLE(6),LDATE(2),XMEAS(100),YMEAS(100),XNUMV(40)
      DATA WE,WEXE,WEYE,WEZE,WEAE,WEBE/2169.8135802,13.2383076,1.0511272
     6-2,-5.7445-5,9.831E-7,3.1650E-8/
      DATA BE,AE,GE,DE,DDE,BDE,PE,HE,ENE/1.93128087240,1.7504+121E-2,5.43
     67E-7,-2.5+1E-8,6.121403E-6,1.1526E-9,1.6053E-10,5.3272E-12,1.7375E
     6-13/
C
C     READ TITLE AND DATE
```

```
C
      READ100,(TITLE(I),I=1,6)
  100 FORMAT(6A10)
      READ120,LDATE(1),LDATE(2)
  120 FORMAT(2A10)
C
C     READ DELTA V AND ABSOLUTE INTENSITY FLAG
C
      READ*,DELTAV,FFA3
      IDELTAV=IFIX(DELTAV)
      IFA3=IFIX(FFA3)
C
C     READ INTERFEROMETER DATA
C
      READ*,FNDP,FNTP,IAFN,SSP
      NDP=IFIX(FNDP)
      NTP=IFIX(FNTP)
C
C     READ ROTEM PRINT CONTROL
C
      READ*,PRIN1
      IPRIN1=IFIX(PRIN1)
      IF(IPRIN1.EQ.0)GO TO 140
      PRINT130,(TITLE(I),I=1,6)
  130 FORMAT(1H1,1X,6A10)
      PRINT135,LDATE(1),LDATE(2)
  135 FORMAT(1H0,1X,2A10)
      PRINT137,NDP,NTP,IAFN,SSP
  137 FORMAT(1H0,1X,*INTERFEROMETER PARAMETERS: NDP=*,I5,4X,*NTP=*,I5,4X
     6,*AFN=*,A2,4X,*SSP=*,F3.1)
      IF(I  .EQ.1)PRINT138,IDELTAV
      IF(IFA3.EQ.0)PRINT139,IDELTAV
  138 FORMAT(1H0,1X,*DELTA V FOR THIS DATA=*,I2,5X,*INTENSITIES ARE ABSO
     6LUTE(WATTS/STER/WAVENUMBER)*)
  139 FORMAT(1H0,1X,*DELTA V FOR THIS DATA=*,I2,5X,*INTENSITIES ARE RELA
     6TIVE*)
C
C     GET THE ROTATIONAL TEMPERATURE
C
  140 CALL ROTEM(IPRIN1,FFN0,TEMP)
C
C     READ VIBDIS PRINT CONTROL
C
      READ*,PRIN2
      IPRIN2=IFIX(PRIN2)
      IF(IPRIN2.EQ.0.OR.IPRIN1.NE.0)GO TO 160
      PRINT130,(TITLE(I),I=1,6)
      PRINT135,LDATE(1),LDATE(2)
      PRINT137,NDP,NTP,IAFN,SSP
      IF(IFA3.EQ.1)PRINT138,IDELTAV
      IF(IFA3.EQ.0)PRINT139,IDELTAV
C
C     GET THE VIBRATIONAL DISTRIBUTION
C
  160 CALL VIBDIS(IPRIN2,XMEAS,YMEAS,NPV,XNUMV,IHIV,YOFFSET,TEMP)
C
C     CHECK FOR A CALCOMP PLOT
```

```
C
      READ*,FPLOT
      IPLOT=IFIX(FPLOT)
      IF(IPLOT.EQ.0)GO TO 1000
C
C     YOU WANTED A PLOT, SO WHICH TYPE?
C
      READ*,OPTION
      IOPTN=IFIX(OPTION)
C
C     HOW BIG?
C
      READ*,FXF,FLXF,CXF,FYE,FLYE,CYE
C
C     CHECK TO SEE IF WAVENUMBERS ARE INCREASING
C
      IF(FXF.LT.FLXF)GO TO 170
      XMIN=FLXF
      XMAX=FXF
      GO TO 180
  170 XMIN=FXF
      XMAX=FLXF
C
C     GENERATE THEORETICAL SPECTRUM
C
  180 CALL SPECGN(XNUMV,IHIV,YOFFSET,TEMP,XMIN,XMAX,XTHERY,YTHERY,NTHRY)
C
C     NOW THAT YOU'VE GOT IT....PLOT IT....
C
      CALL PLOTTOR(XTHERY,YTHERY,NTHRY,XMEAS,YMEAS,NPV,FXF,FLXF,CXF,FYE,
     6FLYE,CYE,IOPTN,LDATE)
 1000 STOP
      END
```

```
      SUBROUTINE ROTEM(IPRNT,FNO,TEMP)
C
C     THIS SUBROUTINE CALCULATES THE ROTATIONAL TEMPERATURE OF HOT
C     CARBON MONOXIDE BY COMPARING THEORETICAL INTENSITIES WITH MEASURED
C     INTENSITIES OF THE R-BRANCH OF THE V'=DELTA V TO V''=0 TRANSITION.
C     THE PROGRAM USES THE METHOD OF LEAST-SQUARES TO DETERMINE THE
C     NUMBER DENSITY IN THE V'=DELTA V LEVEL AND THE ROTATIONAL TEMP-
C     ERATURE OF THE CO.
C
C     DESCRIPTION OF PARAMETERS
C       IPRNT  - DATA PRINTOUT CONTROL (INPUT)
C                +1 PROGRAM PRINTS OUT MEAS. AND CALC. VALUES
C                 0 NO PRINTOUT
C       FNO    - NUMBER DENSITY IN THE V'=DELTA V LEVEL (OUTPUT)
C       TEMP   - ROTATIONAL TEMPERATURE OF THE GAS (OUTPUT)
C
C     OTHER INPUT IS VIA READ STATEMENTS AND COMMONS- THE DATA IS READ
C       IN A LIST DIRECTED READ FORMAT IN PAIRS, IE. X(1),Y(1),X(2),Y(2)
C       ... WHERE X IS THE MEASURED WAVENUMBER AND Y IS THE INTENSITY.
C
C     SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
C       CURFIT - DETERMINES LEAST SQUARES FIT
C       FIO    - CALLED BY CURFIT (SEE CURFIT)
C       FDERIV - CALLED BY CURFIT (SEE CURFIT)
C       MATINV - CALLED BY CURFIT (SEE CURFIT)
C       ESTEIN - CALLED BY FIO
C       BPASS  - CALLED BY FIO
C       F      - CALLED BY ESTEIN
C
C     COMMENTS
C       DIMENSION STATEMENT VALID FOR UP TO 50 DATA POINTS
C     VERSION 03-31-78-1      MAR. 31, 1978       C. DEJOSEPH, JR.
C
      COMMON/Z/NDP,SSP,IAFN,NTP,IDELTAV,IFAB
      COMMON/W/WE,WEXE,WEYE,WEZE,WEAE,WEBE,BE,AE,GE,DE,BDE,BBE,PE,HE,ENE
      DIMENSION WAV(50),FINT(50),PRM(3),DPRM(3),YFNT(50),SIGP(3),SGY(50)
C
C     READ THE NUMBER OF DATA POINTS, THEN THE POINTS, THEN THE STANDARD
C     DEVIATION OF THE MEASURED INTENSITIES. IF STANDARD DEVIATION IS
C     SET TO ZERO, THE FIT IS NOT WEIGHTED.
C
      READ*,NPR,(WAV(I),FINT(I),I=1,NPR),SIGGMA
      MODE=1
      IF(SIGGMA.EQ.0.)MODE=0
C
C     FIND THE LARGEST INTENSITY VALUE, AND SET UP SGY ARRAY
C
      FMAX=FINT(1)
      DO 10 I=1,NPR
      SGY(I)=SIGGMA
      IF(FINT(I).LT.FMAX)GO TO 10
      ISV=I
      FMAX=FINT(I)
   10 CONTINUE
C
C     SET UP INITIAL GUESSES FOR CURFIT (INITIALIZE PRM ARRAY)
C
```

```
C*******THIS IS THE INITIAL GUESS AT ROTATIONAL TEMPERATURE*************
C
      PRM(1)=500.0
C
C***********************************************************************
      PRM(2)=1.
      PRM(2)=FMAX/FIO(WAV,ISV,PRM)
      PRM(3)=0.0
C
C     SET UP INCREMENTS OF PRM FOR DERIVATIVE CALCULATIONS
C
      DPRM(1)=1.0
      DPRM(2)=0.01*PRM(2)
      DPRM(3)=0.01*FMAX
C
C     GET CURFIT
C
      CALL CURFIT(WAV,FINT,SGY,NPR,3,MODE,PRM,DPRM,SIGP,.001,YFNT,CHIQ)
C
C     PREPARE FOR PRINTOUT OR RETURN
C
      FNO=PRM(2)
      TEMP=PRM(1)
      IF(IPRNT.EQ.0)GO TO 100
      PRINT150
  150 FORMAT(1H0,8X,54H****DATA FROM ROTATIONAL TEMPERATURE DETERMINATIO
     6N****)
      IF(MODE.EQ.0)GO TO 12
      PRINT160,MODE,SIGGMA
  160 FORMAT(1H0,1X,*MODE=*,I2,/,2X,*STANDARD DEVIATION ASSUMED FOR THE
     6MEASURED INTENSITIES=*,1PE10.3)
      GO TO 16
   12 PRINT170,MODE
  170 FORMAT(1H0,1X,*MODE=*,I2,5X,*(NO WEIGHTING)*)
   16 PRINT200,TEMP,SIGP(1)
  200 FORMAT(1H0,1X,*ROTATIONAL TEMPERATURE=*,1PE10.3,* DEG.K*,/,2X,*EST
     6IMATED STANDARD DEVIATION=*,E10.3,* DEG.K*)
      PRINT300,IDELTAV,FNO,SIGP(2)
  300 FORMAT(1H0,1X,*NUMBER DENSITY IN THE V=*,I2,* LEVEL=*,1PE10.3,* CM
     6-3*,/,2X,*ESTIMATED STANDARD DEVIATION=*,E10.3,* CM-3*)
      PRINT350,PRM(3),SIGP(3)
  350 FORMAT(1H0,1X,*ZERO OFFSET OF INTENSITIES=*,1PE10.3,* +OR-*,E10.3)
      PRINT400
  400 FORMAT(1H0,1X,*WAVENUMBER*,6X,*MEAS. INTENSITY*,6X,*CALC. INTENSIT
     6Y*,5X,*PERCENT DIFF.*)
      DIFT=0.
      DO 20 J=1,NPR
      DIF=(FINT(J)-YFNT(J))/FINT(J)*100.
      DIFT=DIFT+ABS(DIF)
   20 PRINT500,WAV(J),FINT(J),YFNT(J),DIF
  500 FORMAT(1H ,1X,F6.2,10X,1PE10.3,10X,E10.3,11X,0PF6.1)
      FNPR=NPR
      DIFT=DIFT/FNPR
      PRINT600,DIFT,CHIQ
  600 FORMAT(1H0,1X,*AVERAGE ABSOLUTE ERROR=*,F5.1,* PERCENT*,/,2X,*CHI-
     6SQUARE=*,1PE12.5)
  100 RETURN
```

```
      SUBROUTINE VIBDIS(IPRNT,XMEAS,YMEAS,NPV,VNCAL,IHIV,YOFFSET,TEMP)
C
C     THE PURPOSE OF THIS PROGRAM IS TO CALCULATE THE VIBRATIONAL
C     POPULATION DISTRIBUTION OF CARBON MONOXIDE UNDER DISCHARGE CONDIT-
C     IONS. THE CALCULATION IS DONE BY COMPARING MEASURED SPECTRA FROM
C     EITHER THE FUNDAMENTAL, FIRST OVERTONE, OR SECOND OVERTONE WITH
C     THEORETICAL SPECTRA. THE LEVEL POPULATIONS ARE DETERMINED BY THE
C     METHOD OF LEAST SQUARES USING A MULTIPLE LINEAR REGRESION ROUTINE.
C
C     DESCRIPTION OF PARAMETERS
C       IPRNT   - PRINTOUT CONTROL PARAMETER (INPUT)
C                 0 - NO PRINTOUT
C                 1 - A LINE-PRINTER PLOT OF THE RELATIVE OCCUPATION
C                     NUMBERS AND THE CALCULATED NUMBER DENSITIES IS MADE
C                 2 - A PRINTOUT OF THE CALCULATED COEFFICIENTS FROM
C                     REGRES WITH STATISTICS IS MADE
C                 3 - OPTION 1 + OPTION 2
C       XMEAS   - THE ARRAY OF MEASURED WAVENUMBERS (OUTPUT)
C       YMEAS   - THE ARRAY OF MEASURED INTENSITIES (OUTPUT)
C       NPV     - THE NUMBER OF DATA POINTS USED IN THE FIT (OUTPUT)
C       VNCAL   - THE ARRAY OF CALCULATED LEVEL POPULATIONS (VNCAL(I) IS
C                 THE NUMBER OF MOLECULES IN THE I-1 VIB. LEVEL, OUTPUT)
C       IHIV    - THE HIGHEST VIBRATIONAL LEVEL INCLUDED IN THE FIT (THE
C                 SIZE OF THE VNCAL ARRAY IS IHIV+1, OUTPUT)
C       YOFFSET- CALCULATED OFFSET OF ZERO INTENSITY (OUTPUT)
C       TEMP    - THE ROTATIONAL TEMPERATURE OF THE GAS (INPUT)
C
C     SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
C       REGRES - MULTIPLE LINEAR REGRESION ROUTINE
C       PLOTIT - LINE-PRINTER PLOT ROUTINE
C       MATINV - SYMETRIC MATRIX INVERTER, CALLED BY REGRES
C       FCTN    - INTERMEDIARY BETWEEN REGRES AND FNV, CALLED BY REGRES
C       FNV     - CALCULATES INTENSITY CONTRIBUTIONS FROM DIFFERENT VIB.
C                 LEVELS, CALLED BY FCTN
C       BPASS   - CALCULATES INSTRUMENT FUNCTION, CALLED BY FNV
C       ESTEIN - CALCULATES EINSTEIN A AND B COEFFICIENTS, CALLED BY FNV
C       F       - CALCULATES HERMAN WALLACE FACTORS, CALLED BY ESTEIN
C
C     COMMENTS
C       ADDITIONAL INPUT IS THROUGH COMMONS AND READ STATEMENTS. XMEAS,
C       YMEAS, NPV, IHIV ARE READ FROM CARDS AND SUPPLIED TO THE CALLING
C       ROUTINE THROUGH THE CALL LIST. IPRNT AND TEMP MUST BE SUPPLIED
C       BY THE CALLING ROUTINE. VNCAL IS CALCULATED IN VIBDIS AND IS
C       RETURNED TO THE CALLING ROUTINE THROUGH THE CALL LIST. DIMENSION
C       STATEMENTS VALID FOR NPV UP TO 100 AND IHIV UP TO 39
C     VERSION 12-16-77-1(SPECIAL WEIGHTING)   FEB.24,1977 C.DEJOSEPH, JR.
C
      COMMON/Z/NOP,JSP,IAFN,NTP,IDELTAV,IFAB
      COMMON/W/WE,WEXE,WEYE,WEZE,WEAE,WEBE,BE,AE,GE,DE,DDE,BEE,PE,HE,EHE
      COMMON/SCALIT/NX,NY,NXT,NYT,LINPIN,IGRID
      DIMENSION XMEAS(1),YMEAS(1),VNCAL(1)
      DIMENSION SIGM(100),YFT(100),SIGMAV(40),RR(40),RELN(40),RELOC(40),
     6XXV(40)
      G(V)=V*(WE+V*(-WEXE+V*(WEYE+V*(-WEZE+V*(WEAE-V*WEBE)))))
      HCK=1.43882
C
C     READ THE NUMBER OF DATA POINTS, THEN THE POINTS, THEN THE STANDARD
```

AD-A105 496 UNIVERSAL ENERGY SYSTEMS INC DAYTON OH F/G 7/4
INVESTIGATION OF PLASMA EXCITATION. VOLUME III. ADVANCED OPTICA--ETC(U)
AUG 81 C A DEJOSEPH F33615-77-C-3113
UNCLASSIFIED 707-3-F AFWAL-TR-81-2082-VOL-3 NL

2 OF 2
AD A
105496

END
DATE
FILMED
11-81
DTIC

```
C     DEVIATION OF THE MEASURED INTENSITIES. IF THE STANDARD DEVIATION
C     IS SET TO ZERO, THE FIT IS NOT WEIGHTED
C
      READ*,NPV,(XMEAS(I),YMEAS(I),I=1,NPV),SIGG
      MODE=1
      IF(SIGG.EQ.0.)MODE=0
C
C     SET UP SIGM ARRAY
C
C**********************************************************************
C
C     WEIGHTING FUNCTION IS ROUGHLY 1/INSTRUMENT FUNCTION
C
C**********************************************************************
      DO 20 I=1,NPV
      RFF=-3.2405E7+XMEAS(I)*(1.2315E5+XMEAS(I)*(-5.5590E1+XMEAS(I)*(1.2
     6153E-2-XMEAS(I)*9.0458E-7)))
   20 SIGM(I)=8.2358E6/RFF*SIGG
C
C     READ THE HIGHEST LEVEL INCLUDED IN THE FIT, AND THE CO PARTIAL
C     PRESSURE (TORR)
C
      READ*,IHIV,COPRES
C
C     GET READY TO CALL REGRES
C
      NTT=IHIV+1-IDELTAV
      CALL REGRES(XMEAS,YMEAS,SIGM,NPV,NTT,TEMP,MODE,YFT,A0,VNCAL,SGA0,S
     6IGMAV,RR,RMUL,CHISQ,FTEST)
      YOFFSET=A0
C
C     SINCE VNCAL CONTAINS NUMBERS FROM V=DELTA V TO V=IHIV, LOWER V'S
C     MUST BE CALCULATED AND STORED IN VNCAL
C
      DO 30 J=1,NTT
      K=NTT+IDELTAV-J+1
   30 VNCAL(K)=VNCAL(K-IDELTAV)
C
C     ASSUME THE LOWER LEVELS FOLLOW A TREANOR DISTRIBUTION
C
      V1=FLOAT(IDELTAV)+.5
      V2=V1+1.
      JJ=IDELTAV+1
      A12=(G(V2)-G(V1))*HCK/TEMP
      AKK=ALOG(VNCAL(JJ+1)/VNCAL(JJ))+A12
      DO 40 J=1,IDELTAV
      V3=FLOAT(J-1)+.5
      A13=(G(V1)-G(V3))*HCK/TEMP
   40 VNCAL(J)=VNCAL(JJ)*EXP(-FLOAT(JJ-J)*AKK+A13)
C
C     NOW SET UP OCCUPATION NUMBERS
C
      TOT=0.
      IH=IHIV+1
      DO 50 J=1,IH
   50 TOT=TOT+VNCAL(J)
      DENS=2.6872E19*273./TEMP*COPRES/760.
```

```
      DO 60 J=1,IH
      RELOC(J)=VNCAL(J)/TOT
   60 RELN(J)=RELOC(J)*DENS
C
C     PREPARE FOR PRINTOUT OR RETURN
C
      IF(IPRNT.EQ.0)GO TO 3000
      IF(IPRNT.EQ.1)GO TO 1000
      PRINT500
  500 FORMAT(1H0,7X,56H****DATA FROM VIBRATIONAL DISTRIBUTION DETERMINAT
     6ION****)
      IF(MODE.EQ.0)GO TO 70
      PRINT505,NPV,SIGG
  505 FORMAT(1H0,1X,*NUMBER OF DATA POINTS=*,I3,/,2X,*STANDARD DEVIATION
     6 ASSUMED FOR THE MEASURED INTENSITIES=*,1PE10.3)
      GO TO 80
   70 PRINT510,NPV
  510 FORMAT(1H0,1X,*NUMBER OF DATA POINTS=*,I3,5X,*(NO WEIGHTING)*)
   80 PRINT525
  525 FORMAT(1H0,1X,*WAVENUMBER*,6X,*MEAS. INTENSITY*,6X,*CALC. INTENSIT
     6Y*,5X,*PERCENT DIFF.*)
      DIFT=0.
      DO 110 I=1,NPV
      DIF=(YMEAS(I)-YFT(I))/YMEAS(I)*100.
      DIFT=DIFT+ABS(DIF)
  110 PRINT530,XMEAS(I),YMEAS(I),YFT(I),DIF
  530 FORMAT(1H ,1X,F8.2,10X,1PE10.3,10X,E10.3,11X,0PF6.1)
      FNPV=NPV
      DIFT=DIFT/FNPV
      PRINT535,DIFT,CHISQ
  535 FORMAT(1H0,1X,*AVERAGE ABSOLUTE ERROR=*,F6.1,* PERCENT*,/,2X,*CHI-
     6SQUARE=*,1PE12.5)
      PRINT540,IHIV,TEMP
  540 FORMAT(1H0,1X,*HIGHEST VIBRATIONAL LEVEL INCLUDED IN FIT=*,I3,/,2X
     6,*ASSUMED ROTATIONAL TEMPERATURE=*,1PE10.3,* DEG.K*)
      PRINT550
  550 FORMAT(1H0,19X,32H****COEFFICIENTS FROM REGRES****)
      PRINT560,A0,SGA0
  560 FORMAT(1H0,1X,*ZERO OFFSET OF INTENSITIES=*,1PE10.3,* +OR-*,E10.3)
      PRINT570
  570 FORMAT(1H0,1X,*UPPER V*,5X,*COEF.*,6X,*EST. STD. DEV.*,6X,*LINEAR
     6CORRELATION COEF.*)
      DO 120 I=1,NIT
      J=I+IDELTAV
      K=J-1
  120 PRINT580,K,VNCAL(J),SIGMAV(I),RR(I)
  580 FORMAT(1H ,4X,I2,5X,1PE10.3,5X,E10.3,10X,E10.3)
      PRINT590,RMUL,FTEST
  590 FORMAT(1H0,1X,*MULTIPLE LINEAR CORRELATION COEF.=*,1PE10.3,/,2X,*V
     6ALUE OF FTEST=*,E10.3)
      IF(IPRNT.EQ.2)GO TO 3000
 1000 PRINT700
  700 FORMAT(1H0,1X,*VIBRATIONAL POPULATION DATA--IF INTENSITIES ARE ABS
     6OLUTE, LAST COLUMN IS ABSOLUTE*)
      PRINT710
  710 FORMAT(1H0,1X,*VIB. LEVEL*,3X,*REL. OCCUPATION NO.*,4X,*REL. NO. D
     6ENSITY*,5X,*NO. IN LEVEL*)
```

```
            YMIN=YMAX=RELOC(1)
            DO 130 I=1,IH
            L=I-1
            PRINT720,L,RELOC(I),RELN(I),VNCAL(I)
        720 FORMAT(1H ,5X,I2,12X,1PE10.3,12X,E10.3,10X,E10.3)
            XXV(I)=L
            YMIN=AMIN1(YMIN,RELOC(I))
        130 YMAX=AMAX1(YMAX,RELOC(I))
            XMIN=0.
            XMAX=FLOAT(IH-1)
            MMODE=12
            CALL PLOTIT(XXV,RELOC,IH,1H*,XMIN,XMAX,YMIN,YMAX,MMODE,2)
       3000 RETURN
            END
```

```
      SUBROUTINE SPECGN(XNV,LEVEL,YOFFSET,TEMP,WMIN,WMAX,WOUT,YOUT,NN)
C
C     THE PURPOSE OF THIS PROGRAM IS TO GENERATE A THEORETICAL EMISSION
C     SPECTRUM FROM CARBON MONOXIDE. THE PROGRAM IS NORMALLY USED IN
C     CONJUNCTION WITH THE AFAPL/POD FOURIER TRANSFORM SPECTROMETER,
C     THEREFORE SUCH QUANTITIES AS INSTRUMENT RESOLUTION, DATA POINT
C     SPACING, ETC. ARE MATCHED TO THOSE OF THE INSTRUMENT BY THE COMMON
C     /Z/. THE OUTPUT IS TWO ARRAYS WOUT AND YOUT WHICH ARE THE WAVE-
C     NUMBERS AND INTENSITIES OF THE CALCULATED SPECTRUM.
C
C     DESCRIPTION OF PARAMETERS
C       XNV     - THE ARRAY OF NUMBER DENSITIES FOR THE VARIOUS
C                 VIBRATIONAL LEVELS OF CO (GROUNDSTATE=XNV(1))
C       LEVEL   - THE NUMBER OF THE HIGHEST LEVEL SUPPLIED BY XNV. (IF
C                 LEVEL=J, THE ARRAY SIZE FOR XNV=J+1)
C       YOFFSET- CONSTANT ADDED TO EACH INTENSITY CALCULATED
C       TEMP    - THE ROTATIONAL TEMPERATURE OF THE GAS
C       WMIN    - THE LOWEST WAVENUMBER DESIRED FOR THE CALCULATION
C       WMAX    - THE HIGHEST WAVENUMBER DESIRED FOR THE CALCULATION
C       WOUT    - THE ARRAY OF OUTPUT WAVENUMBERS
C       YOUT    - THE ARRAY OF OUTPUT INTENSITIES
C       NN      - THE NUMBER OF DATA POINTS GENERATED
C
C     SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
C       FNV(X,I,J,TEMP)
C         CALCULATES THE INTENSITY CONTRIBUTION FROM VARIOUS VIB. LEVELS
C
C     COMMENTS
C       WMIN AND WMAX ARE LIMITS ON THE DATA. THE SPACING OF THE WOUT
C       ARRAY IS DETERMINED BY COMMON/Z/ SO THAT WOUT MIGHT NOT CONTAIN
C       WMIN AND/OR WMAX.
C     VERSION 03-15-76-2       MAR. 15, 1976        G. D. JOSEPH, JR.
C
      COMMON/Z/NDP,SSP,IAFN,NTF,IDELTAV,IFAB
      COMMON/W/WE,WEXE,WEYE,WEZE,WEAE,WEBE,BE,AE,GE,DE,DDE,BBE,PE,HE,ENE
      DIMENSION WOUT(1),YOUT(1),XNV(1)
      DIMENSION WVC(40)
      G(V)=V*(WE+V*(-WEXE+V*(WEYE+V*(-WEZE+V*(WEAE-V*WEBE)))))
      FV(V,R)=R*(R+1)*((BE+V*(-AE+V*(GE-V*DE)))+R*(R+1)*((-DDE+V*(BBE-PE
     6*V))+R*(R+1)*(HE-V*ENE)))
C
C     SET UP LIMITS ON WOUT ARRAY
C
      FNTP=NTP
      IMIN=IFIX(WMIN*SSP*FNTP/15798./2.)+1
      IMAX=IFIX(WMAX*SSP*FNTP/15798./2.)-1
      NN=IMAX-IMIN+1
      IF(NN.GT.1998)GO TO 200
      JSTOP=LEVEL-IDELTAV+1
C
C     LOCATE BAND CENTERS FOR EACH VIB. LEVEL
C
      DO 10 J=1,JSTOP
      VLO=FLOAT(J-1)+.5
      VUP=VLO+FLOAT(IDELTAV)
   10 WVC(J)=G(VUP)-G(VLO)
C
```

```
C     SET UP THE WOUT AND YOUT ARRAYS
C
      NSLIDE=4
      DO 70 I=1,NN
      WOUT(I)=13796.*2./SSP/FNTP*FLOAT(IMIN+I-1)
      YOUT(I)=YOFFSET
      DO 30 J=1,JSTOP
      JVC=J
      IF(WOUT(I).GT.WVC(J))GO TO 40
   30 CONTINUE
   40 IF(JVC.EQ.JSTOP)JVC=JSTOP-2
      IF(JVC.LT.3)JVC=3
      JVMIN=JVC-NSLIDE
      JVMAX=JVC+NSLIDE
      IF(JVMIN.LT.1)JVMIN=1
      IF(JVMAX.GT.JSTOP)JVMAX=JSTOP
      DO 60 J=JVMIN,JVMAX
C
C     WATCH OUT FOR THE DIFFERENCE IN INDEX DEFINITIONS BETWEEN FNV AND
C     XNV.
C
      JJ=J+IDELTAV
   60 YOUT(I)=YOUT(I)+XNV(JJ)*FNV(WOUT,I,J,TEMP)
   70 CONTINUE
C
C     THAT SHOULD DO IT.........
C
      GO TO 1000
  200 PRINT210
  210 FORMAT(1H0,1X,*NUMBER OF POINTS REQUESTED ON PLOT EXCEEDS DIMENSIO
     6N STATEMENTS---EXECUTION HALTED*)
      STOP
 1000 RETURN
      END
```

```
      SUBROUTINE PLOTTOR(XTHERY,YTHERY,NTHERY,XDATA,YDATA,NDATA,FXF,FLXF
     6,DXF,FYL,FLYL,DYL,IOPTN,LABEL)
C
C     THE PURPOSE OF THIS PROGRAM IS TO PLOT BOTH THE THEORETICAL
C     SPECTRUM AND THE MEASURED DATA POINTS FOR CARBON MONOXIDE EMISSION
C
C     DESCRIPTION OF PARAMETERS
C       XTHERY - THE ARRAY OF WAVENUMBERS FOR THE THEORETICAL SPECTRUM
C       YTHERY - THE ARRAY OF INTENSITIES FOR THE THEORETICAL SPECTRUM
C       NTHERY - THE NUMBER OF POINTS TO BE PLOTTED IN THE THEOR. SPECT.
C       XDATA  - THE ARRAY OF MEASURED WAVENUMBERS
C       YDATA  - THE ARRAY OF MEASURED INTENSITIES
C       NDATA  - THE NUMBER OF MEASURED DATA POINTS
C       FXF    - THE FIRST WAVENUMBER ON THE PLOT AXIS
C       FLXF   - THE LAST WAVENUMBER ON THE PLOT AXIS
C       DXF    - THE CHANGE IN WAVENUMBER FOR THE X-AXIS (WAVE./INCH)
C       FYL    - THE FIRST INTENSITY VALUE ON THE PLOT AXIS
C       FLYL   - THE LAST INTENSITY VALUE ON THE PLOT AXIS
C       DYL    - THE CHANGE IN INTENSITY FOR THE Y-AXIS (UNITS/INCH)
C       IOPTN  - CONTROLS PLOT OPTIONS
C                0 - NORMAL PLOT SEQUENCE
C                1 - NO DATA PLOTTED, ONLY THEORETICAL SPECTRUM
C                2 - Y-AXIS IS SCALED TO 6 INCHES, FYL, DCT. IGNORED
C                3 - NO DATA IS PLOTTED, Y-AXIS SCALED TO 5 INCHES
C       LABEL  - TWO WORD ARRAY FOR PUTTING 20 CHARACTER TITLE ON PLOT
C
C     COMMENTS
C       THIS VERSION OF PLOTTOR DESTROYS THE ARRAYS XTHERY AND YTHERY.
C       IF IT IS DESIRED NOT TO DESTROY THESE ARRAYS, REMOVE THE C FROM
C       COLUMN 1 OF THE FIRST DIMENSION STATEMENT AND REMOVE THE COMMON
C       BLOCK /FF/.
C
C     VERSION 02-26-78-1       FEB. 26, 1978       C. DEJOSEPH, JR.
C
      COMMON/Z/NOP,SOP,IAFN,NTP,IDELTAV,IFAU
C*********************************************************************
      COMMON/FF/XT(2000),YT(2000)
C     DIMENSION XT(2000),YT(2000)
C*********************************************************************
      DIMENSION XTHERY(1),YTHERY(1),XDATA(1),YDATA(1),LABEL(2)
      DATA YL/5.0/
C
C     ESTABLISH THE ORIGIN AT X=0,Y=.9
      CALL PLOT(0.,-1.,-3)
      CALL PLOT(0.,.9,-3)
C
      NN2=NTHERY+2
      NN1=NTHERY+1
      IF(IOPTN-1)30,30,10
C
C     SCALE Y-AXIS
C
   10 YMIN=YMAX=YTHERY(1)
      DO 15 I=1,NTHERY
      YMAX=AMAX1(YMAX,YTHERY(I))
   15 YMIN=AMIN1(YMIN,YTHERY(I))
      IF(IOPTN.EQ.3)GO TO 25
```

```
      DO 25 I=1,NDATA
      YMAX=AMAX1(YMAX,YDATA(I))
   20 YMIN=AMIN1(YMIN,YDATA(I))
   25 DYPIN=(YMAX-YMIN)/YL
      YT(NN2)=DYPIN
      YT(NN1)=YMIN
      GO TO 40
   30 YL=(FLYE-FYE)/CYE
      YMIN=FYE
      YT(NN2)=CYE
      YT(NN1)=FYE
   40 YMAXG=YMIN+YT(NN2)*IFIX(YL)
C
C     SCALE X-AXIS
C
      XMIN=FXF
      XMAXG=FLXF
      IF(FXF.GT.FLXF)XMIN=FLXF
      IF(FXF.GT.FLXF)XMAXG=FXF
      DXPIN=CXF
      XL=(FLXF-FXF)/CXF
      XT(NN2)=DXPIN
      XT(NN1)=FXF
C
C     DRAW AXES
C
      CALL AXIS(0.,0.,11HWAVENUMBERS,-11,XL,0.,XT(NN1),XT(NN2))
      IF(IFAB.NE.3)GO TO 45
      CALL AXIS(0.,0.,19HINTENSITY(RELATIVE),19,YL,90.,YT(NN1),YT(NN2))
      GO TO 47
   45 CALL AXIS(0.,0.,32HINTENSITY(WATTS/STER/WAVENUMBER),32,YL,90.,YT(N
     6N1),YT(NN2))
C
C      SET UP TEMPORARY ARRAYS-TRUNCATE EXTREME VALUES
C
   47 DO 50 J=1,NTHERY
      XT(J)=XTHERY(J)
      IF(XT(J).LT.XMIN)XT(J)=XMIN
      IF(XT(J).GT.XMAXG)XT(J)=XMAXG
      YT(J)=YTHERY(J)
      IF(YT(J).LT.YMIN)YT(J)=YMIN
   50 IF(YT(J).GT.YMAXG)YT(J)=YMAXG
C
C     CONNECT ARRAY POINTS
C
      CALL LINE(XT,YT,NTHERY,1,0,0)
C
C     PLOT MEASURED DATA?
C
      IF(IOPTN.EQ.1.OR.IOPTN.EQ.3)GO TO 100
      N2=NDATA+2
      N1=NDATA+1
      XT(N2)=XT(NN2)
      XT(N1)=XT(NN1)
      YT(N2)=YT(NN2)
      YT(N1)=YT(NN1)
      DO 56 J=1,NDATA
```

```
      XT(J)=XDATA(J)
      IF(XT(J).LT.XMIN)XT(J)=XMIN
      IF(XT(J).GT.XMAXG)XT(J)=XMAXG
      YT(J)=YDATA(J)
      IF(YT(J).LT.YMIN)YT(J)=YMIN
   50 IF(YT(J).GT.YMAXG)YT(J)=YMAXG
C
C     PLOT THE MEASURED DATA POINTS
C
      L=5
      CALL LINE(XT,YT,NDATA,1,-1,L)
C
C     LABEL PLOT
C
  100 YTOP=YL+.5
      CALL SYMBOL(1.0,YTOP,.245,LABEL(1),0.,10)
      CALL SYMBOL(999.,999.,.245,LABEL(2),0.,10)
      CALL PLOTE
      RETURN
      END
```

```
C     SUBROUTINE CURFIT
C
C     PURPOSE
C       MAKE A LEAST-SQUARES FIT TO A NON-LINEAR FUNCTION WITH A LINEAR-
C       IZATION OF THE FITTING FUNCTION.
C
C     USAGE
C       CALL CURFIT(X,Y,SIGMAY,NPTS,NTERMS,MODE,A,DELTAA,SIGMAA,FLAMDA,
C       YFIT,CHISQR)
C
C     DESCRIPTION OF PARAMETERS
C       X      - ARRAY OF DATA POINTS FOR THE INDEPENDENT VARIABLE
C       Y      - ARRAY OF DATA POINTS FOR THE DEPENDENT VARIABLE
C       SIGMAY - ARRAY OF STANDARD DEVIATIONS FOR Y DATA POINTS
C       NPTS   - NUMBER OF PAIRS OF DATA POINTS
C       NTERMS - NUMBER OF PARAMETERS
C       MODE   - DETERMINES METHOD OF WEIGHTING LEAST SQUARES FIT
C                +1 (INSTRUMENTAL) WEIGHT=1./SIGMAY(I)**2
C                 0 (NO WEIGHTING) WEIGHT=1.
C                -1 (STATISTICAL)  WEIGHT=1./Y(I)
C       A      - ARRAY OF PARAMETERS
C       SIGMAA - ARRAY OF STANDARD DEVIATIONS FOR PARAMETERS A
C       DELTAA - ARRAY OF INCREMENTS FOR PARAMETERS A
C       FLAMDA - PORTION OF GRADIENT SEARCH INCLUDED
C       YFIT   - ARRAY OF CALCULATED VALUES OF Y
C       CHISQR - REDUCED CHI SQUARE FOR THE FIT
C
C     SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
C       FIT(X,I,A)
C          EVALUATES THE FITTING FUNCTION FOR THE ITH DATA POINT
C       FCHISQ(Y,SIGMAY,NPTS,NFREE,MODE,YFIT)
C          EVALUATES REDUCED CHI SQUARE FOR FIT TO DATA
C       FDERIV(X,I,A,DELTAA,NTERMS,DERIV)
C          EVALUATES THE DERIVATIVES OF THE FITTING FUNCTION FOR THE ITH
C          TERM WITH RESPECT TO EACH PARAMETER
C       MATINV(NTERMS,DET)
C          INVERTS A SYMMETRIC TWO-DIMENSIONAL MATRIX OF DEGREE NTERMS
C          AND CALCULATES ITS DETERMINANT
C
C     COMMENTS
C       DIMENSION STATEMENT VALID FOR NTERMS UP TO 3
C       SET FLAMDA=.001 AT BEGINNING OF SEARCH
C       IF ANALYTIC DERIVATIVES ARE USED DELTAA IS NOT NEEDED
C       INITIAL GUESSES FOR PARAMETERS A MUST BE MADE
C     VERSION 02-26-78-1       FEB. 26, 1978       C. DEJOSEPH, JR.
C
      SUBROUTINE CURFIT(X,Y,SIGMAY,NPTS,NTERMS,MODE,A,DELTAA,SIGMAA,FLAM
     6DA,YFIT,CHISQR)
      DOUBLE PRECISION ARRAY,CHECK
      COMMON/Z/NUP,SSP,IAFN,NTP,IDELTAV,IFAB
      COMMON/W/WE,WEXE,WEYE,WEZE,WEAE,WEBE,BE,AE,GE,DE,DDE,DBE,PE,HE,NE
      COMMON/AA/ARRAY(40,40)
      DIMENSION X(1),Y(1),SIGMAY(1),A(1),DELTAA(1),SIGMAA(1),YFIT(1)
      DIMENSION ALPHA(3,3),BETA(3),DERIV(3),B(3)
      NFREE=NPTS-NTERMS
      IT=0
      IF(NFREE)13,13,15
```

```
   13 CHISQR=0.
      GO TO 115
   15 ITF=0
      DO 20 J=1,NTERMS
      BETA(J)=0.
      DO 20 K=1,J
   20 ALPHA(J,K)=0.
      DO 50 I=1,NPTS
      IF(MODE)22,27,29
   22 IF(Y(I))25,27,23
   23 WEIGHT=1./Y(I)
      GO TO 30
   25 WEIGHT=1./(-Y(I))
      GO TO 30
   27 WEIGHT=1.
      GO TO 30
   29 WEIGHT=1./SIGMAY(I)/SIGMAY(I)
   30 CONTINUE
      CALL FDERIV(X,I,A,DELTAA,NTERMS,DERIV)
      DO 45 J=1,NTERMS
      BETA(J)=BETA(J)+WEIGHT*(Y(I)-FIC(X,I,A))*DERIV(J)
      DO 45 K=1,J
   45 ALPHA(J,K)=ALPHA(J,K)+WEIGHT*DERIV(J)*DERIV(K)
   50 CONTINUE
      DO 53 J=1,NTERMS
      DO 53 K=1,J
   53 ALPHA(K,J)=ALPHA(J,K)
      DO 62 I=1,NPTS
   62 YFIT(I)=FIC(X,I,A)
      CHISQ1=FCHISQ(Y,SIGMAY,NPTS,NFREE,MODE,YFIT)
   71 DO 74 J=1,NTERMS
      DO 73 K=1,NTERMS
   73 ARRAY(J,K)=DBLE(ALPHA(J,K)/SQRT(ALPHA(J,J)*ALPHA(K,K)))
   74 ARRAY(J,J)=DBLE(1.0+FLAMDA)
      CALL MATINV(NTERMS,DET)
      DO 84 J=1,NTERMS
      B(J)=A(J)
      DO 84 K=1,NTERMS
   84 B(J)=B(J)+BETA(K)*ARRAY(J,K)/SQRT(ALPHA(J,J)*ALPHA(K,K))
      DO 92 I=1,NPTS
   92 YFIT(I)=FIC(X,I,B)
      CHISQR=FCHISQ(Y,SIGMAY,NPTS,NFREE,MODE,YFIT)
      IF(CHISQ1-CHISQR)95,101,101
   95 FLAMDA=10.*FLAMDA
      ITF=ITF+1
      IF(ITF.LE.10)GO TO 71
      GO TO 111
  101 DO 103 J=1,NTERMS
      IF(B(J).EQ.0.)GO TO 103
      IF(A(J).EQ.0.)GO TO 103
      IF(B(J)*A(J).GT.0.)GO TO 102
      JSNG=J
      GO TO 109
  102 CHECK=(A(J)-B(J))/B(J)
      CHECK=DABS(CHECK)
      IF(CHECK-1.0D-03)103,103,105
  103 CONTINUE
```

```
      104 NOUT=1
          GO TO 106
      105 NOUT=0
          IT=IT+1
          IF(IT-25)106,105,113
      106 DO 107 J=1,NTERMS
      107 A(J)=B(J)
          FLAMDA=FLAMDA/10.
          IF(FLAMDA.LT.0.001)FLAMDA=0.001
          IF(NOUT.EQ.0)GO TO 15
          DO 108 J=1,NTERMS
      108 SIGMAA(J)=DSQRT(ARRAY(J,J)/ALPHA(J,J))
          GO TO 115
      103 PRINT1030,JSNG
     1030 FORMAT(* PARAMETER *,I2,* CHANGED SIGN---EXECUTION HALTED.*,/,* TR
         6Y NEW INITIAL GUESSES.*)
          STOP
      111 PRINT1110
     1110 FORMAT(* FLAMDA HAS BEEN INCREASED TEN TIMES, CHI SQUARE IS STILL*
         6,/,* INCREASING---EXECUTION HALTED.*)
          STOP
      113 PRINT1130
     1130 FORMAT(* 25 ITERATIONS COMPLETED, CONVERGENCE CRITERIA NOT MET---E
         6XECUTION HALTED*)
          GO TO 104
      115 RETURN
          END
```

```
      SUBROUTINE MATINV
C
C     PURPOSE
C       INVERT A SYMETRIC MATRIX AND CALCULATE ITS DETERMINANT
C
C     USAGE
C     CALL MATINV(NORDER,DET)
C
C     DESCRIPTION OF PARAMETERS
C       NORDER - DEGREE OF MATRIX(ORDER OF DETERMINANT)
C       DET    - DETERMINANT OF INPUT MATRIX
C
C     COMMENTS
C       DIMENSION STATEMENTS VALID FOR NORDER UP TO 40
C       THE ARRAY IS CARRIED THROUGH THE COMMON/AA/
C     VERSION 12-16-77-1       DEC. 15, 1977      C. DEJOSEPH, JR.
C
      SUBROUTINE MATINV(NORDER,DET)
      DOUBLE PRECISION ARRAY,AMAX,SAVE
      COMMON/AA/ARRAY(40,40)
      DIMENSION IK(40),JK(40)
      DET=1.
      DO 100 K=1,NORDER
C
C     FIND LARGEST ELEMENT ARRAY(I,J) IN REST OF MATRIX
C
      AMAX=0.0D0
   21 DO 30 I=K,NORDER
      DO 30 J=K,NORDER
      IF(DABS(AMAX)-DABS(ARRAY(I,J)))24,24,30
   24 AMAX=ARRAY(I,J)
      IK(K)=I
      JK(K)=J
   30 CONTINUE
C
C     INTERCHANGE ROWS AND COLUMNS TO PUT AMAX IN ARRAY(K,K)
C
      IF(AMAX)41,32,41
   32 DET=0.0
      GO TO 140
   41 I=IK(K)
      IF(I-K)21,51,43
   43 DO 50 J=1,NORDER
      SAVE=ARRAY(K,J)
      ARRAY(K,J)=ARRAY(I,J)
   50 ARRAY(I,J)=-SAVE
   51 J=JK(K)
      IF(J-K)21,61,53
   53 DO 60 I=1,NORDER
      SAVE=ARRAY(I,K)
      ARRAY(I,K)=ARRAY(I,J)
   60 ARRAY(I,J)=-SAVE
   61 DO 70 I=1,NORDER
      IF(I-K)63,70,63
   63 ARRAY(I,K)=-ARRAY(I,K)/AMAX
   70 CONTINUE
      DO 80 I=1,NORDER
```

```
      DO 80 J=1,NORDER
      IF(I-K) 74,80,74
   74 IF(J-K) 75,80,75
   75 ARRAY(I,J)=ARRAY(I,J)+ARRAY(I,K)*ARRAY(K,J)
   80 CONTINUE
      DO 90 J=1,NORDER
      IF(J-K) 83,90,83
   83 ARRAY(K,J)=ARRAY(K,J)/AMAX
   90 CONTINUE
      ARRAY(K,K)=1./AMAX
  100 DET=DET*AMAX
C
C     RESTORE ORDERING OF MATRIX
C
      DO 130 L=1,NORDER
      K=NORDER-L+1
      J=IK(K)
      IF(J-K) 111,111,105
  105 DO 110 I=1,NORDER
      SAVE=ARRAY(I,K)
      ARRAY(I,K)=-ARRAY(I,J)
  110 ARRAY(I,J)=SAVE
  111 I=JK(K)
      IF(I-K) 130,130,113
  113 DO 120 J=1,NORDER
      SAVE=ARRAY(K,J)
      ARRAY(K,J)=-ARRAY(I,J)
  120 ARRAY(I,J)=SAVE
  130 CONTINUE
  140 RETURN
      END
```

```
      FUNCTION FCHISQ
C
C     PURPOSE
C       EVALUATE REDUCED CHI SQUARE FOR FIT TO DATA
C       FCHISQ=SUM((Y-YFIT)**2)/NFREE
C
C     USAGE
C       RESULT=FCHISQ(Y,SIGMAY,NPTS,NFREE,MODE,YFIT)
C
C     DESCRIPTION OF PARAMETERS
C       Y      - ARRAY OF DATA POINTS
C       SIGMAY - ARRAY OF STANDARD DEVIATIONS FOR DATA POINTS
C       NPTS   - NUMBER OF DATA POINTS
C       NFREE  - NUMBER OF DEGREES OF FREEDOM
C       MODE   - DETERMINES METHOD OF WEIGHTING LEAST SQUARES FIT
C                +1 (INSTRUMENTAL) WEIGHT=1./SIGMAY(I)**2
C                 0 (NO WEIGHTING) WEIGHT=1.
C                -1 (STATISTICAL) WEIGHT=1./Y(I)
C       YFIT   - ARRAY OF CALCULATED VALUES OF Y
C     VERSION 12-15-77-1      DEC. 15, 1977     C. DEJOSEPH, JR.
C
      FUNCTION FCHISQ(Y,SIGMAY,NPTS,NFREE,MODE,YFIT)
      DOUBLE PRECISION CHISQ,WEIGHT
      DIMENSION Y(1),SIGMAY(1),YFIT(1)
      CHISQ=0.
      IF (NFREE)13,13,20
   13 FCHISQ=0.
      GO TO 40
C
C     ACCUMULATE CHI SQUARE
C
   20 DO 30 I=1,NPTS
      IF(MODE)22,27,29
   22 IF(Y(I))25,27,23
   23 WEIGHT=1./Y(I)
      GO TO 30
   25 WEIGHT=1./(-Y(I))
      GO TO 30
   27 WEIGHT=1.
      GO TO 30
   29 WEIGHT=1./SIGMAY(I)/SIGMAY(I)
   30 CHISQ=CHISQ+WEIGHT*(Y(I)-YFIT(I))*(Y(I)-YFIT(I))
C
C     DIVIDE BY THE NUMBER OF DEGREES OF FREEDOM
C
      FREE=NFREE
      FCHISQ=CHISQ/FREE
   40 RETURN
      END
```

SYMBOLIC REFERENCE MAP (R=1)

```
      FUNCTION FIG(X,I,A)
C
C     THIS FUNCTION CALCULATES THE INTENSITY FROM THE TRANSITION
C     V'=DELTA V TO V''=0 FOR CARBON MONOXIDE AS A FUNCTION OF WAVE-
C     NUMBER. ONLY THE CONTRIBUTION TO THE INSTRUMENT BANDPASS FROM THE
C     R-BRANCH IS CONSIDERED.
C
C     DESCRIPTION OF PARAMETERS:
C       X - ARRAY OF DATA POINTS FOR THE WAVENUMBERS
C       I - INDEX OF DATA POINTS
C       A - ARRAY OF PARAMETERS TO BE FIT: A(1)=ROTATIONAL TEMPERATURE
C                                          A(2)=NO. DENSITY IN V=DELTA V
C                                          A(3)=ZERO OFFSET
C     SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED:
C       FUNCTION BPASS(NDP,SSP,IAFN,VNUG,VNU)
C         CALCULATES THE INSTRUMENT BANDPASS
C       SUBROUTINE ESTEIN(IDELTAV,IVLOWER,M,IHOLD,W,A,B)
C         CALCULATES THE EINSTEIN A AND B COEFFICIENTS
C     VERSION 03-01-78-1       MAR. 01, 1978       C. DEJOSEPH, JR.
C
      COMMON/Z/NDP,SSP,IAFN,NTP,IDELTAV,IFAB
      COMMON/W/WE,WEXE,WEYE,WEZE,WEAE,WEBE,BE,AE,GE,DE,DDE,BBE,PE,HE,ENE
      DIMENSION X(1),A(3)
      DATA H,CL,PI,HCK/6.62619650E-34,2.997924562E10,3.14159265358993,1.4
     6338632/
      G(V)=V*(WE+V*(-WEXE+V*(WEYE+V*(-WEZE+V*(WEAE-V*WEBE)))))
      FV(V,R)=R*(R+1)*((BE+V*(-AE+V*(GE-V*DE)))+R*(R+1)*((-DDE+V*(BBE-PE
     6*V))+R*(R+1)*(HE-V*ENE)))
      FIG=0.0
      IF(A(1).LE.0.0)GO TO 30
      XI=X(I)
      IVLO=0
      IVUP=IVLO+IDELTAV
      VLO=FLOAT(IVLO)+.5
      VUP=FLOAT(IVUP)+.5
      T1=G(VUP)-G(VLO)
      CALL ESTEIN(IDELTAV,IVLO,1,0,T1,AA,BB)
      Q=1.
      HCKT=HCK/A(1)
      CON1=A(2)*H*CL/4./PI
      BV=BE+VUP*(-AE+VUP*(GE-VUP*DE))
C
C     EMPIRICALLY, THE LIMIT ON THE SUM OF ROTATIONAL LEVELS IS FOUND
C     AS FOLLOWS
C
      JMAX=5*IFIX(0.59*SQRT(A(1)/BV))+1
      DO 20 M=1,JMAX
      RM=M
      RM1=M-1
      W=T1+FV(VUP,RM)-FV(VLO,RM1)
      CALL ESTEIN(IDELTAV,IVLO,M,1,W,AA,BB)
      EX=EXP(-HCKT*FV(VUP,RM))
      FIG=FIG+W*AA*(2.*RM+1.)*EX*BPASS(NDP,SSP,IAFN,XI,W)
   20 Q=Q+(2.*RM+1.)*EX
      FIG=FIG/Q*CON1+A(3)
   30 RETURN
      END
```

```
      SUBROUTINE FDERIV
C
C     PURPOSE
C       EVALUATES DERIVATIVES OF FIB(X,I,A) FOR LEAST-SQUARES SEARCH.
C
C     USAGE
C       CALL FDERIV(X,I,A,DELTAA,NTERMS,DERIV)
C
C     DESCRIPTION OF PARAMETERS
C       X      - ARRAY OF DATA POINTS FOR INDEPENDENT VARIABLE
C       I      - INDEX OF DATA POINTS
C       A      - ARRAY OF PARAMETERS
C       DELTAA - ARRAY OF PARAMETER INCREMENTS
C       NTERMS - NUMBER OF PARAMETERS
C       DERIV  - DERIVATIVES OF FUNCTION
C
C     SUBROUTINES AND FUNCTION SUBROUTINES REQUIRED
C       FUNCTION BPASS(NDP,SSP,IAFN,VNUO,VNU)
C         CALCULATES THE INSTRUMENT BANDPASS
C       SUBROUTINE ESTEIN(IDELTAV,IVLOWER,M,IHOLD,W,A,B)
C         CALCULATES THE EINSTEIN A AND B COEFFICIENTS
C     VERSION 03-01-78-1      MAR. 01, 1978       C. DEJOSEPH, JR.
C
      SUBROUTINE FDERIV(X,I,A,DELTAA,NTERMS,DERIV)
      COMMON/Z/NDP,SSP,IAFN,NTP,IDELTAV,IFAB
      COMMON/W/WE,WEXE,WEYE,WEZE,WEAE,WEBE,BE,AE,GE,DE,DDE,BBE,PE,HE,ENE
      DIMENSION X(1),A(3),DELTAA(1),DERIV(3)
      DATA H,CL,PI,HCK/6.62519656E-34,2.997924562E10,3.14159265358,1.4
     6388327/
      G(V)=V*(WE+V*(-WEXE+V*(WEYE+V*(-WEZE+V*(WEAE-V*WEBE)))))
      FV(V,R)=R*(R+1)*((BE+V*(-AE+V*(GE-V*DE)))+R*(R+1)*((-DDE+V*(BBE-PE
     6*V))+R*(R+1)*(HE-V*ENE)))
      DERIV(1)=DERIV(2)=0.0
      IF(A(1).LE.0.0)GO TO 33
      A11=1./A(1)
      XI=X(I)
      IVLO=0
      IVUP=IVLO+IDELTAV
      VLO=FLOAT(IVLO)+.5
      VUP=FLOAT(IVUP)+.5
      T1=G(VUP)-G(VLO)
      CALL ESTEIN(IDELTAV,IVLO,1,0,T1,AA,BB)
      Q=1.
      Q1=0.0
      HCKT=HCK*A11
      CON1=H*CL/4./PI
      BV=BE+VUP*(-AE+VUP*(GE-VUP*DE))
C
C     EMPIRICALLY, THE LIMIT ON THE SUM OF ROTATIONAL LEVELS IS FOUND
C     AS FOLLOWS
C
      JMAX=5*IFIX(0.39*SQRT(A(1)/BV))+1
      DO 20 M=1,JMAX
      RM=M
      RM1=M-1
      FVUP=FV(VUP,RM)
      W=T1+FVUP-FV(VLO,RM1)
```

```
      ROTJ=2.*RM+1.
      CALL ESTEIN(IDELTAV,IVLO,M,1,W,AA,BB)
      EX=EXP(-HCKT*FVUP)
      FII=W*AA*ROTJ*EX*BPASS(NUP,SSP,IAFN,XI,W)
      DERIV(2)=DERIV(2)+FII
      DERIV(1)=DERIV(1)+FVUP*HCKT*A11*FII
      Q1=Q1+ROTJ*EX*FVUP*HCKT*A11
   20 Q=Q+ROTJ*EX
      DERIV(1)=(DERIV(1)-Q1*DERIV(2)/Q)/Q*A(2)*CON1
      DERIV(2)=DERIV(2)*CON1/Q
      DERIV(3)=1.0
   30 RETURN
      END
```

```
      SUBROUTINE REGRES
C
C     PURPOSE
C       MAKE A MULTIPLE LINEAR REGRESSION FIT TO DATA WITH A SPECIFIED
C       FUNCTION WHICH IS LINEAR IN COEFFICINTS
C
C     USAGE
C       CALL REGRES(X,Y,SIGMAY,NPTS,NTERMS,T,MODE,YFIT,A0,A,SIGMA0
C       SIGMAA,R,RMUL,CHISQR,FTEST)
C
C     DESCRIPTION OF PARAMETERS
C       X       - ARRAY OF DATA POINTS FOR INDEPENDENT VARIABLE
C       Y       - ARRAY OF DATA POINTS FOR DEPENDENT VARIABLE
C       SIGMAY  - ARRAY OF STANDARD DEVIATIONS FOR Y DATA POINTS
C       NPTS    - NUMBER OF PAIRS OF DATA POINTS
C       NTERMS  - NUMBER OF COEFFICIENTS
C       T       - A PARAMETER FOR USE IN FCTN
C       MODE    - DETERMINES METHOD OF WEIGHTING LEAST-SQUARES FIT
C                 +1 (INSTRUMENTAL) WEIGHT(I) = 1./SIGMAY**2
C                  0 (NO WEIGHTING) WEIGHT(I) = 1.
C                 -1 (STATISTICAL)  WEIGHT(I) = 1./Y(I)
C       YFIT    - ARRAY OF CALCULATED VALUES OF Y
C       A0      - CONSTANT TERM
C       A       - ARRAY
C       SIGMA0  - STANDARD DEVIATION OF A0
C       SIGMAA  - ARRAY OF STANDARD DEVIATIONS FOR COEFFICIENTS
C       R       - ARRAY OF LINEAR CORRELATION COEFFICIENTS
C       RMUL    - MULTIPLE LINEAR CORRELATION COEFFICIENTS
C       CHISQR  - REDUCED CHI SQUARE FOR THE FIT
C       FTEST   - VALUE OF F FOR TEST OF FIT
C
C     SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
C       FNV(X,I,J,T)
C          EVALUATES THE FUNCTION FOR THE JTH TERM AND ITH DATA POINT
C        AND T IS A PARAMETER FOR USE IN FNV
C       MATINV(NTERMS,DET)
C          INVERTS A SYMMETRIC TWO-DIMENSIONAL MATRIX OF DEGREE NTERMS
C          AND CALCULATES ITS DETERMINANT
C
C     COMMENTS
C       THIS PROGRAM IS A SLIGHTLY MODIFIED VERSION OF ONE APPEARING IN
C       BEVINGTON.  DIMENSION STATEMENTS ARE VALID FOR NPTS UP TO 100
C       AND NTERMS UP TO 40.
C     VERSION 12-16-77-1      DEC. 16, 1977      J. JOSEPH, JR.
C
      SUBROUTINE REGRES(X,Y,SIGMAY,NPTS,NTERMS,T,MODE,YFIT,A0,A,SIGMA0,S
     6IGMAA,R,RMUL,CHISQR,FTEST)
      DOUBLE PRECISION ARRAY,SUM,YMEAN,SIGMA,CHISQ,XMEAN,SIGMAX
      DOUBLE PRECISION FCXM
      COMMON/Z/NOP,SSP,IAFN,NTP,IDELTAV,IFAB
      COMMON/W/WE,WEXE,WEYE,WEZE,WEAE,WEBE,BE,AE,GE,DE,DDE,BBE,PE,HE,ENE
      COMMON/AA/ARRAY(40,40)
      COMMON/FF/FCTN(100,40)
      DIMENSION X(1),Y(1),SIGMAY(1),YFIT(1),A(1),SIGMAA(1),R(1)
      DIMENSION WEIGHT(100),XMEAN(40),SIGMAX(40)
C
C     INITIALIZE SUMS AND ARRAYS
```

```
      C
            SUM=YMEAN=SIGMA=CHISQ=0.0D0
            RMUL=0.0
            DO 17 I=1,NPTS
         17 YFIT(I)=0.0
            DO 25 J=1,NTERMS
            XMEAN(J)=SIGMAX(J)=0.0D0
            R(J)=A(J)=SIGMAA(J)=0.0
            DO 25 K=1,NTERMS
         25 ARRAY(J,K)=0.0
      C
      C     ACCUMULATE WEIGHTED SUMS
      C
            DO 50 I=1,NPTS
            IF(MODE)32,37,39
         32 IF(Y(I))35,37,33
         33 WEIGHT(I)=1./Y(I)
            GO TO 41
         35 WEIGHT(I)=1./(-Y(I))
            GO TO 41
         37 WEIGHT(I)=1.
            GO TO 41
         39 WEIGHT(I)=1./SIGMAY(I)/SIGMAY(I)
         41 SUM=SUM+WEIGHT(I)
            YMEAN=YMEAN+WEIGHT(I)*Y(I)
            DO 44 J=1,NTERMS
            FCTN(I,J)=FNV(X,I,J,T)
         44 XMEAN(J)=XMEAN(J)+WEIGHT(I)*FCTN(I,J)
         50 CONTINUE
            YMEAN=YMEAN/SUM
            DO 53 J=1,NTERMS
         53 XMEAN(J)=XMEAN(J)/SUM
            FNPTS=NPTS
            WMEAN=SUM/FNPTS
            DO 57 I=1,NPTS
         57 WEIGHT(I)=WEIGHT(I)/WMEAN
      C
      C     ACCUMULATE MATRICES R AND ARRAY
      C
            DO 67 I=1,NPTS
            SIGMA=SIGMA+WEIGHT(I)*(Y(I)-YMEAN)*(Y(I)-YMEAN)
            DO 67 J=1,NTERMS
            FCXM=FCTN(I,J)-XMEAN(J)
            SIGMAX(J)=SIGMAX(J)+WEIGHT(I)*FCXM*FCXM
            R(J)=R(J)+WEIGHT(I)*FCXM*(Y(I)-YMEAN)
            DO 67 K=1,J
         67 ARRAY(J,K)=ARRAY(J,K)+WEIGHT(I)*FCXM*(FCTN(I,K)-XMEAN(K))
            FREE1=NPTS-1
            SIGMA=DSQRT(SIGMA/FREE1)
            DO 78 J=1,NTERMS
            SIGMAX(J)=DSQRT(SIGMAX(J)/FREE1)
            R(J)=R(J)/(FREE1*SIGMAX(J)*SIGMA)
            DO 78 K=1,J
            ARRAY(J,K)=ARRAY(J,K)/(FREE1*SIGMAX(J)*SIGMAX(K))
         78 ARRAY(K,J)=ARRAY(J,K)
      C
      C     INVERT SYMMETRIC MATRIX
```

```
      C
            CALL MATINV(NTERMS,DET)
            IF(DET)101,91,101
         91 A0=SIGMA0=RMUL=CHISQR=FTEST=0.0
            GO TO 150
      C
      C     CALCULATE COEFFICIENTS, FIT, AND CHI SQUARE
      C
        101 A0=YMEAN
            DO 108 J=1,NTERMS
            DO 104 K=1,NTERMS
        104 A(J)=A(J)+R(K)*ARRAY(J,K)
            A(J)=A(J)*SIGMA/SIGMAX(J)
            A0=A0-A(J)*XMEAN(J)
            DO 108 I=1,NPTS
        108 YFIT(I)=YFIT(I)+A(J)*FCTN(I,J)
            DO 113 I=1,NPTS
            YFIT(I)=YFIT(I)+A0
        113 CHISQ=CHISQ+WEIGHT(I)*(Y(I)-YFIT(I))*(Y(I)-YFIT(I))
            FREEN=NPTS-NTERMS-1
            CHISQR=CHISQ*WMEAN/FREEN
      C
      C     CALCULATE UNCERTAINTIES
      C
            IF(MODE)122,124,122
        122 VARNCE=1./WMEAN
            GO TO 131
        124 VARNCE=CHISQR
        131 DO 133 J=1,NTERMS
            SIGMAA(J)=ARRAY(J,J)*VARNCE/(FREE1*SIGMAX(J)*SIGMAX(J))
            SIGMAA(J)=SQRT(SIGMAA(J))
        133 RMUL=RMUL+A(J)*R(J)*SIGMAX(J)/SIGMA
            FREEJ=NTERMS
            FTEST=(RMUL/FREEJ)/((1.-RMUL)/FREEN)
            RMUL=SQRT(RMUL)
            SIGMA0=VARNCE/FNPTS
            DO 145 J=1,NTERMS
            DO 145 K=1,NTERMS
        145 SIGMA0=SIGMA0+VARNCE*XMEAN(J)*XMEAN(K)*ARRAY(J,K)/(FREE1*SIGMAX(J)
           6*SIGMAX(K))
            SIGMA0=SQRT(SIGMA0)
        150 RETURN
            END
```

```
      FUNCTION FNV(X,I,J,TEMP)
C
C     THIS FUNCTION CALCULATES THE INTENSITY CONTRIBUTION FROM THE
C     TRANSITION V'=(J-1)+DELTA V TO V''=(J-1) FOR CARBON MONOXIDE AS A
C     FUNCTION OF WAVENUMBER. THE ACTUAL POWER DENSITY (WATTS/CM3) IS
C     GIVEN BY THE PRODUCT OF FNV AND THE NUMBER DENSITY IN THE UPPER
C     LEVEL. THE CALCULATED CONTRIBUTION TAKES INTO ACCOUNT THE INSTRU-
C     MENT BANDPASS AND THE ROTATIONAL TEMPERATURE OF THE GAS.
C
C     DESCRIPTION OF PARAMETERS
C       X       - ARRAY OF DATA POINTS FOR WAVENUMBERS
C       I       - INDEX OF WAVENUMBERS
C       J       - VIBRATIONAL LEVEL INDEX, VLOWER=J-1
C       TEMP    - ROTATIONAL TEMPERATURE OF THE GAS
C
C     SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
C       FUNCTION BPASS(NDP,SSP,IAFN,VNU0,VNU)
C         CALCULATES THE INSTRUMENT BANDPASS
C       SUBROUTINE ESTEIN(IDELTAV,IVLOWER,N,IHOLD,W,A,B)
C         CALCULATES THE EINSTEIN A AND B COEFFICIENTS
C     VERSION 12-21-77-1       DEC. 21, 1977        C. DEJOSEPH, JR.
C
      COMMON/Z/NDP,SSP,IAFN,NTF,IDELTAV,IFAB
      COMMON/W/WE,WEXE,WEYE,WEZE,WEAE,WEBE,BE,AE,GE,DE,DDE,BBE,PE,HE,ENE
      DIMENSION X(1)
C
C     CON1=H*C/4/PI
      DATA CON1,HCK/1.58079352E-24,1.438832/
      G(V)=V*(WE+V*(-WEXE+V*(WEYE+V*(-WEZE+V*(WEAE-V*WEBE)))))
      FV(V,R)=R*(R+1)*((BE+V*(-AE+V*(GE-V*DE)))+R*(R+1)*((-DDE+V*(BBE-PE
     6*V))+R*(R+1)*(HE-V*ENE)))
      FNV=0.
      XI=X(I)
      IVLO=J-1
      IVUP=IVLO+IDELTAV
      VLO=FLOAT(IVLO)+.5
      VUP=FLOAT(IVUP)+.5
      T1=G(VUP)-G(VLO)
      CALL ESTEIN(IDELTAV,IVLO,1,0,T1,AA,BB)
      Q=1.
      HCKT=HCK/TEMP
      BV=BE+VUP*(-AE+VUP*(GE-VUP*DE))
C
C     EMPIRICALLY, THE LIMIT ON THE SUM OF ROTATIONAL LEVELS IS FOUND
C     AS FOLLOWS
C
      JMAX=5*IFIX(0.93*SQRT(TEMP/BV))
      JJMAX=2*JMAX+2
C
C     NOW SUM 'EM
C
      DO 100 K=1,JJMAX
      M=K-JMAX-1
      IF(M)10,100,20
   10 RLO=-M
      RUP=RLO-1.
      FVU=FV(VUP,RUP)
```

```
      EX=EXP(-HCKT*FVU)
      GO TO 30
   20 RLO=M-1
      RUP=RLO+1.
      FVU=FV(VUP,RUP)
      EX=EXP(-HCKT*FVU)
      Q=Q+(2.*RUP+1.)*EX
   30 W=T1+FVU-FV(VLO,RLO)
      CALL ESTEIN(IDELTAV,IVLO,M,1,W,AA,BB)
      FNV=FNV+W*AA*(2.*RUP+1.)*EX*BPASS(NUP,SSP,IAFN,XI,W)
  100 CONTINUE
      FNV=FNV/Q*CON1
      RETURN
      END
```

```
      SUBROUTINE ESTEIN(IDELTAV,IVLOWER,M,IHOLD,W,A,B)
C
C     THIS SUBROUTINE CALCULATES THE EINSTEIN 'A' AND 'B' COEFFICIENTS
C     FOR A GIVEN VALUE OF DELTA V, LOWER VIB. LEVEL, AND ROTATIONAL
C     INDEX M. THIS INDEX IS DEFINED BY:
C
C                          M = -J'' = -J' - 1      FOR P BRANCH   M=-1,-2,-3..
C
C                          M = J'' + 1 = J'        FOR R BRANCH   M=+1,+2,+3..
C
C     WHERE J'' IS THE LOWER J VALUE AND J' IS THE UPPER. THE PROGRAM
C     CAN BE USED FOR DELTA V=1,2, OR 3 AND LOWER V UP TO 24. HIGHER
C     VALUES OF VLOWER ARE POSSIBLE, BUT ACCURACY BECOMES QUESTIONABLE.
C     THE CALCULATIONS ARE BASED ON THE WORK OF YOUNG AND EACHUS-J.CHEM
C     PHYS-VOL 44-NO.11(1966).
C
C     DESCRIPTION OF VARIABLES:
C        IDELTAV - DELTA V FOR THE TRANSITION
C        IVLOWER - LOWER VIBRATIONAL QUANTUM NUMBER
C        M       - ROTATIONAL INDEX (DEFINED ABOVE)
C        IHOLD   - IF IHOLD=1, THE PROGRAM ASSUMES VLOWER AND IDELTAV
C                  ARE THE SAME AS IN THE PREVIOUS CALL.
C        W       - WAVENUMBER OF THE TRANSITION (INPUT BY USER)
C        A       - EINSTEIN 'A' COEFFICIENT (OUTPUT)
C        B       - EINSTEIN 'B' COEFFICIENT (OUTPUT)
C
C     SUBROUTINES REQUIRED:
C        FUNCTION F(IDELTAV,IVLOWER,M)
C             THIS FUNCTION CALCULATES THE HERMAN-WALLACE FACTORS FOR CO
C     VERSION 01-05-76-1       JAN. 5, 1976        C. DEJOSEPH, JR.
C
      DIMENSION RO(3),COF(3,4)
      DATA RO/3.1042E-18,6.59525E-18,0.0063635E-15/
      DATA (COF(1,K),K=1,4)/-3.56255E-5,-5.54558E-4,-7.1333E-5,-5.5574E-6/
      DATA (COF(2,K),K=1,4)/-3.7520E-3,2.6384E-2,4.7454E-5,7.4363E-5/
      DATA (COF(3,K),K=1,4)/-1.6747E-3,5.0901E-2,6.3522E-4,2.2342E-6/
C
C     CONA=64*PI**4/3/H       CONB=1/3/PI/H/C
      DATA CONA,CONB/3.136123862E29,2.002973158E14/
C
C     CALCULATE THE V-DEPENDENT PART OF THE RADIAL MATRIX ELEMENT
C
      IF(IHOLD.EQ.1)GO TO 20
      VL=IVLOWER
      ID=IDELTAV
      PROD=1.0
   10 DV=ID
      PROD=PROD*(VL+DV)/DV
      ID=ID-1
      IF(ID.GE.1)GO TO 10
      ID=IDELTAV
      YTERM=COF(ID,1)+VL*(COF(ID,2)+VL*(COF(ID,3)+VL*COF(ID,4)))+1.
      RV=RO(ID)*RO(ID)*PROD*YTERM
      RVA=CONA*RV
      RVB=RVA*CONB
C
C     NOW CONSIDER THE ROTATIONAL DEPENDENCE. TWO QUANTITIES NEEDED ARE
```

```
C     THE HONL-LONDON FACTOR AND THE UPPER AND LOWER LEVEL DEGENERACIES.
C     DEFINE THE RATIO OF UPPER TO LOWER LEVEL DEGENERACY AS DUL. DEFINE
C     THE RATIO OF HONL-LONDON FACTOR TO UPPER LEVEL DEGENERACY AS SU.
C     IT CAN BE SHOWN:
C
   20 RM2=2*M+1
      DUL=RM2/FLOAT(2*M-1)
      SU=FLOAT(M)/RM2
C
C     NOW CONTINUE WITH THE ROTATIONAL DEPENDENCE
C
      HWSU=SU*F(IDELTAV,IVLOWER,M)
C
C     HERE COME THE A AND B COEF., A IS IN 1/SEC, B IS IN CM**2/ERG/SEC
C
      A=RVA*W*W*W*HWSU
      B=RVB*HWSU*DUL
      RETURN
      END
```

```
      FUNCTION F(IDELTAV,IVLOWER,M)
C
C     THIS FUNCTION CALCULATES THE HERMAN-WALLACE FACTORS FOR CARBON
C     MONOXIDE AS A FUNCTION OF DELTA V, LOWER VIBRATIONAL LEVEL, AND
C     ROTATIONAL INDEX M. THIS INDEX IS DEFINED BY:
C
C                         M = -J'' =-J' - 1        FOR P BRANCH
C
C                         M = J'' + 1 = J'         FOR R BRANCH
C
C     WHERE J'' IS THE LOWER J VALUE AND J' IS THE UPPER. THE PROGRAM
C     CAN BE USED FOR DELTA V=1,2, OR 3 AND LOWER V=24. HIGHER VALUES
C     OF VLOWER ARE POSSIBLE, BUT ACCURACY BECOMES QUESTIONABLE. THIS
C     PROGRAM USES THE CONSTANTS FROM STANFORD UNIVERSIYT REPORT
C     SU-IPP REPORT NO.622, BY DAVID JAMES BENDER, MARCH 1975.
C     VERSION 12-16-77-1        DEC. 16, 1977       S. DEJOSEPH, JR.
C
C
      DIMENSION C(3,6,4),X(6),R(6)
      DATA (C(1,K,1),K=1,6)/-2.531E-3,-5.509E-3,-8.473E-3,-1.185E-2,-1.5
     651E-2,-1.957E-2/
      DATA (C(2,K,1),K=1,6)/4.071E-2,4.215E-2,3.79.E-2,3.259E-2,2.803E-2
     6,2.394E-2/
      DATA (C(3,K,1),K=1,6)/1.026E-1,9.234E-2,8.340E-2,7.554E-2,6.774E-2
     6,6.191E-2/
      DATA (C(1,K,2),K=1,6)/7.010E-4,6.608E-4,4.531E-4,2.755E-4,3.139E-5
     6,-3.145E-4/
      DATA (C(2,K,2),K=1,6)/3.164E-3,3.040E-3,2.925E-3,2.817E-3,2.715E-3
     6,2.515E-3/
      DATA (C(3,K,2),K=1,6)/7.912E-3,7.257E-3,6.755E-3,6.347E-3,5.623E-3
     6,5.303E-3/
      DATA (C(1,K,3),K=1,6)/-2.096E-5,-3.108E-5,-3.556E-5,-3.972E-5,-4.2
     660E-5,-4.250E-5/
      DATA (C(2,K,3),K=1,6)/7.346E-5,5.977E-5,4.465E-5,2.715E-5,6.279E-6
     6,-1.539E-5/
      DATA (C(3,K,3),K=1,6)/4.500E-4,3.996E-4,3.558E-4,3.153E-4,2.753E-4
     6,2.412E-4/
      DATA (C(1,K,4),K=1,6)/1.039E-7,-7.357E-6,-3.532E-7,-7.738E-7,-1.45
     699E-6,-2.240E-6/
      DATA (C(2,K,4),K=1,6)/4.395E-6,4.257E-6,4.141E-6,3.973E-6,3.749E-6
     6,3.403E-6/
      DATA (C(3,K,4),K=1,6)/2.166E-5,2.055E-5,1.955E-5,1.839E-5,1.635E-5
     6,1.801E-5/
      DATA X/0.,5.,10.,15.,20.,24./
C
C     THE HERMAN-WALLACE FACTORS CAN BE CALCULATED FOR VLOWER=0,5,10,15,
C     20,24. FOR VALUES OF VLOWER DIFFERENT FROM THESE, THE FACTORS ARE
C     CALCULATED USING AN INTERPOLATION/EXTRAPOLATION ROUTINE TAKEN
C     FROM BEVINGTON. NOTE: AFTER TRYING MANY DIFFERENT INTERPOLATION
C     SCHEMES, LINEAR WAS CHOSEN.
C
      NTERMS=2
      ID=IDELTAV
      IV=IVLOWER
      XIN=IV
      XM=M
      XM=XM/10.
```

```
      DO 8 J=1,6
    8 R(J)=1.0+XM*(C(ID,J,1)+XM*(C(ID,J,2)+XM*(C(ID,J,3)+XM*C(ID,J,4))))
      DO 19 I=1,6
      IF(XIN-X(I))13,17,19
   13 I1=I-1
      GO TO 21
   17 YOUT=R(I)
      GO TO 80
   19 CONTINUE
      I1=5
   21 I2=I1+1
      YOUT=R(I1)+(XIN-X(I1))/(X(I2)-X(I1))*(R(I2)-R(I1))
   80 F=YOUT
      RETURN
      END
```

```
      FUNCTION BPASS(NDP,SSP,IAFN,VNU0,VNU)
C
C     THIS FUNCTION CALCULATES THE INSTRUMENT BANDPASS FOR THE AFAPL
C     FOURIER TRANSFORM SPECTROMETER AS A FUNCTION OF VNU-VNU0.
C
C     INPUT PARAMETERS:
C          NDP  - THE NUMBER OF DATA POINTS TAKEN BY THE SPECTROMETER
C          SSP  - THE SAMPLE SPACING OF THE DATA POINTS IN UNITS OF HALF-
C                 WAVELENGTH OF THE HELIUM-NEON LASER.
C          IAFN - THE APODIZATION FUNCTION USED IN THE FOURIER TRANSFORM
C                 OF THE DATA. PERMISSIBLE VALUES OF AFN ARE:
C                    BX - BOXCAR APODIZATION
C                    TI - TRIANGULAR APODIZATION
C                    HG - HAPP-GENZEL APODIZATION
C          VNU0 - WAVENUMBER OF BANDPASS CENTER
C          VNU  - WAVENUMBER AT WHICH RELATIVE BANDPASS IS DESIRED
C     VERSION 01-10-78-1       JAN. 10, 1978       C. DEJOSEPH, JR.
C
      DATA IBX,ITI,IHG/2HBX,2HTI,2HHG/
      DATA PI/3.14159265358979/
C
C     CON1=0.46/0.54
      DATA CON1/0.85185185185/
      FLNG=0.5*SSP*6.32391517E-05*FLOAT(NDP)
      Z1=2.*PI*(VNU-VNU0)*FLNG
      IF(Z1.EQ.0.0)GO TO 30
      Z2=SIN(Z1)
      IF(IAFN.EQ.ITI)GO TO 10
      IF(IAFN.EQ.IHG)GO TO 20
      BPASS=Z2/Z1
      RETURN
   10 Z3=SIN(Z1/2.)
      Z11=1./Z1
      BPASS=Z3*Z3*Z11*Z11*4.0
      RETURN
   20 IF(ABS(Z1).EQ.PI)GO TO 25
      Z11=1./Z1
      BPASS=Z2*Z11*(1.0+CON1/(PI*PI*Z11*Z11-1.))
      RETURN
   25 BPASS=CON1/2.
      RETURN
   30 BPASS=1.0
      RETURN
      END
```

```
      DO 8 J=1,6
    8 R(J)=1.0+XM*(C(ID,J,1)+XM*(C(ID,J,2)+XM*(C(ID,J,3)+XM*C(ID,J,4))))
      DO 19 I=1,6
      IF(XIN-X(I))13,17,19
   13 I1=I-1
      GO TO 21
   17 YOUT=R(I)
      GO TO 80
   19 CONTINUE
      I1=5
   21 I2=I1+1
      YOUT=R(I1)+(XIN-X(I1))/(X(I2)-X(I1))*(R(I2)-R(I1))
   80 F=YOUT
      RETURN
      END
```

APPENDIX III

```
      PROGRAM TRACER(INPUT,OUTPUT)
C
C     THE PURPOSE OF THIS PROGRAM IS TO CALCULATE THE PARTIAL PRESSURES
C     OF VARIOUS INFRARED ABSORBING SPECIES SEEN IN CO2 LASER GAS MIXES.
C     THE PROGRAM IS FOR USE WITH THE AFAPL/POD FOURIER TRANSFORM
C     SPECTROMETER AND LONG PATH ABSORPTION CELL. THE INPUT DATA
C     INCLUDES INTERFEROMETER PARAMETERS, MOLECULAR WEIGHT OF THE ABSORB-
C     ING SPECIES, LINE STRENGTH, VARIOUS BROADENING COEFFICIENTS FOR
C     THE LINE, PARTIAL PRESSURES OF THE MAJOR SPECIES IN THE GAS, AND
C     THE MEASURED PEAK TRANSMITTANCE OF THE LINE. VOIGT PROFILES ARE
C     ASSUMED FOR THE ABSORBING LINES.
C
C     SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED
C       SUBROUTINE SEEKER1(NDP,SSP,IAFN,WO,S,DHW,FGMW,SLFB,T,PP)
C         CALCULATES PARTIAL PRESSURE OF THE ABSORBING SPECIES
C       SUBROUTINE FOLD1(NDP,SSP,IAFN,WO,W,S,DHW,PBHW,PGAS,PLNGTH,T)
C         FOLDS AN FTS BANDPASS FUNCTION WITH AN EXPONENTIAL OF A VOIGT
C         PROFILE.
C       FUNCTION VOIGT(X,Y)
C         CALCULATES A VOIGT PROFILE
C       FUNCTION BPASS1(NDP,SSP,IAFN,VNUO,VNU)
C         CALCULATES A NORMALIZED BANDPASS FUNCTION FOR AN INTERFEROMETER
C
C     WITH THE EXCEPTION OF THE FIRST CARD, ALL CARDS ARE READ IN
C     THE LIST DIRECTED READ FORMAT OF THE CDC6600
C
C     DATA CARDS
C       FIRST CARD  - COLUMNS 1-60 FOR A TITLE
C       SECOND CARD - INTERFEROMETER PARAMETERS
C                     1ST NUMBER - NUMBER OF DATA POINTS TAKEN BY THE
C                                  SPECTROMETER
C                     2ND NUMBER - SAMPLE SPACING OF DATA POINTS IN HALF-
C                                  WAVELENGTHS OF THE HE-NE LASER
C                     3RD NUMBER - HOLLERITH CHARACTERS DESCRIBING APOD-
C                                  IZATION FUNCTION
C                                   "BX" - BOXCAR APOD.
C                                   "TI" - TRIANGULAR APOD.
C                                   "HG" - HAPP-GENZEL APOD.
C       THIRD CARD  - PARTIAL PRESSURES OF THE MAJOR SPECIES (TORR)
C                     1ST NUMBER - PARTIAL PRESSURE OF CO2
C                     2ND NUMBER - PARTIAL PRESSURE OF N2
C                     3RD NUMBER - PARTIAL PRESSURE OF HE
C       FOURTH CARD - COMPLETE DESCRIPTION OF THE ABSORBING LINE
C                     1ST NUMBER - UP TO FIVE HOLLERITH CHARACTERS TO
C                                  NAME THE ABSORBING SPECIES
C                     2ND NUMBER - THE MOLECULAR (OR ATOMIC) WEIGHT OF
C                                  THE SPECIES
C                     3RD NUMBER - THE WAVENUMBER OF THE LINE
C                     4TH NUMBER - THE LINE STRENGTH (CM-2 ATM-1)
C                     5TH NUMBER - THE SELF BROADENING COEFFICIENT
C                                  (CM-1 ATM-1)
C                     6TH NUMBER - THE CO2 BROADENING COEF. (CM-1 ATM-1)
C                     7TH NUMBER - THE N2 BROADENING COEF. (CM-1 ATM-1)
C                     8TH NUMBER - THE HE BROADENING COEF. (CM-1 ATM-1)
C       FIFTH CARD  - MEASURED TRANSMITTANCE DATA
C                     1ST NUMBER - NUMBER OF TRANSMITTANCE MEASUREMENTS
C                                  FOR THE DESCRIBED CONDITIONS
```

```
C                                   (UP TO 10)
C                     2ND NUMBER - THIS NUMBER THRU MTH NUMBER ON THE
C                                  CARD ARE FOR THE TRANSMITTANCE VALUES
C                                  (PER CENT)
C          SIXTH CARD  - CONTROL PARAMETER FOR READING ANOTHER DATA SET
C                        THE PARAMETER MAY HAVE THE FOLLOWING VALUES
C                          0 - STOP (MUST BE INCLUDED AT SOME POINT)
C                          1 - READ A NEW DATA SET STARTING WITH THE THIRD
C                              CARD ABOVE AND ENDING WITH ANOTHER CONTROL
C                              PARAMETER CARD (4 CARDS)
C                          2 - READ A NEW DATA SET STARTING WITH THE 4TH
C                              CARD (3 CARDS)
C                          3 - READ AN ENTIRE NEW DATA SET STARTING WITH A
C                              NEW TITLE CARD
C       COMMENTS
C         PATHLENGTH IS ASSUMED TO BE 20.25 METERS. TEMPERATURE IS ASSUMED
C         TO BE 296 DEG. K.
C
C       VERSION 03-03-80-1      MAR. 03, 1980       C. DEJOSEPH, JR.
C
        DIMENSION TR(10),TITLE(6)
        DATA PATH/2025./
        DATA APR/6.5356625E-10/
C
C       READ IN TITLE AND INTERFEROMETER DATA
C
      1 READ10,(TITLE(I),I=1,6)
     10 FORMAT(6A10)
        READ*,NDP,SSP,IAFN
        FNDP=NDP
C
C       PRINT TITLE, INTERFEROMETER DATA, AND HEADERS
C
        PRINT30,(TITLE(I),I=1,6)
     30 FORMAT(1H1,6A10)
        ISSP=SSP
        PRINT40,NDP,ISSP,IAFN
     40 FORMAT(1H0,*INTERFEROMETER PARAMETERS: NDP=*,I7,4X,*SSP=*,I3,4X,*A
       6FN= *,A2)
        PRINT50
     50 FORMAT(1H0,*SPECIES*,2X,*WAVENUM*,3X,*LINE STRENGTH*,3X,*HE PRES*,
       62X,*N2 PRES*,2X,*CO2 PRES*,2X,*SPECIES PRES*,2X,*TOTAL PRES*,2X,*P
       6.B.H.W.*,4X,*TRANS*)
        PRINT60
     60 FORMAT(1H ,10X,*(CM-1)*,4X,*(CM-2 ATM-1)*,4X,*(TORR)*,3X,*(TORR)*,
       63X,*(TORR)*,6X,*(TORR)*,7X,*(TORR)*,5X,*(CM-1)*,6X,*(%)*)
C
C       READ IN DATA
C
     70 READ*,PCO2,PN2,PHE
        ISK=0
     80 READ*,ISP,WMW,WO,S,BSELF,BCO2,BN2,BHE
        READ*,NT,(TR(I),I=1,NT)
        READ*,IPRIN
        IF(ISP.EQ.ISK)GO TO 95
        IF(ISK.EQ.0)GO TO 90
     85 IF(IC.EQ.1)GO TO 90
```

```
      FIC=IC
      PRAV=PREL/FIC
      SIGR=SQRT((PRELS-FIC*PRAV*PRAV)/(FIC-1.))
      PRINT115,ISK,IC,PRAV,SIGR
      IF(IPRIN.EQ.0)STOP
      IF(IPRIN.EQ.1)GO TO 70
      IF(IPRIN.EQ.3)GO TO 1
   90 PREL=0.
      PRELS=0.
      IC=0
      ISK=ISP
   95 CONTINUE
C
C     CALCULATE PARTIAL PRESSURE- GET READY FOR SEEKER1
C
      FGHW=(PCO2*BCO2+PN2*BN2+PHE*BHE)/760.
      DHW=3.58E-7*SQRT(296./WMW)*WO
C*********************FINITE APERTURE CORRECTION************************
      APRC=WO*FNDP*APR
      NDP=FNDP/SQRT(1+APRC*APRC)
C**********************************************************************
      DO 100 J=1,NT
      TX=TR(J)
      CALL SEEKER1(NDP,SSP,IAFN,WO,S,DHW,FGHW,BSELF,TX,PX)
      PTOT=PX+PCO2+PN2+PHE
      PBHW=FGHW+PX*BSELF/760.
      FRAC=PX/PTOT
      PREL=PREL+FRAC
      PRELS=PRELS+FRAC*FRAC
      IC=IC+1
  100 PRINT110,ISP,WO,S,PHE,PN2,PCO2,PX,PTOT,PBHW,TX
  110 FORMAT(1H ,1X,A5,2X,F8.2,5X,1PE10.3,4X,0PF6.1,3X,F6.1,3X,F6.1,5X,1
     6PE9.2,5X,0PF6.1,3X,1PE10.3,2X,0PF7.2)
  115 FORMAT(1H ,*THE AVERAGE RELATIVE CONCENTRATION OF *,A4,
     6*CALCULATED FROM THE ABOVE*,I2,* MEASUREMENTS IS*,1PE10.3,3X,*STD.
     6 DEV.=*,E10.3)
      IF(IPRIN-1)120,121,118
  118 IF(IPRIN-2)80,80,119
  119 IF(IC-1)1,1,85
  120 IF(IC-1)130,130,85
  121 IF(IC-1)70,70,85
  130 STOP
      END
```